CERTAIN CHEMICAL REACTIONS AT REDUCED TEMPERATURES AND RELATED PROBLEMS OF ENERGY TRANSFER

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INTRODUCTION

Considerable progress in chemical kinetics and the mechanism of gas phase reactions was made in the 'twenties and 'thirties of this century. An important contribution was made, in particular, by the development of the activated complex theory and the theory of chain reactions, together with the related concept of the part played by free radicals in chemical gas reactions. The present concepts of gas phase reactions, though not yet complete, are on the whole satisfactory. The knowledge of kinetics of liquid phase reactions is far from being adequate, but in certain regions of this field our concepts are sufficiently clear. As to kinetics of reactions in solids, only the first steps have been taken towards an elucidation of the solid phase reaction mechanisms.

I am far from claiming that this paper makes a substantial advance in the knowledge of solid phase reactions. The field has recently attracted the attention of many experimenters in a number of countries and of theorists, but to a lesser degree, I am afraid. Various experimental studies on this subject were carried out at the Institute of Chemical Physics during the last two to three years[1–11]. I shall discuss the results of them here, together with the related hypotheses which have to be verified by further experiments. I shall also consider some of the data reported in literature, but without aiming at a full survey.

Let us begin with the most simple reaction, that of radical recombination in solids at low temperatures.

RECOMBINATION OF RADICALS

The generation of free radicals by irradiation of the condensed phase opened up wide possibilities for investigating this reaction and solid phase reaction in general, particularly at low temperatures.

Radicals are very mobile in gases and liquids, and their recombination is so fast that the accumulation of high concentrations of these particles is prevented; their persistence after irradiation is quite excluded.

Completely different conditions prevail in solids at sufficiently low temperatures, when the diffusion of free radicals becomes impossible. However, as radicals are formed by breaking of molecular bonds, they are initially close together and may well recombine. This consideration would seem to prevent the formation of appreciable radical concentrations in solids as well. However, it is known from experiments by American scientists, the first to tackle this problem, that considerable concentrations of free radicals may be obtained by low-temperature solid phase irradiation; the amount of broken bonds constitute fractions of one per cent of the over-all number of bonds[12]. This fact may be due to at least two reasons: (*i*) for the majority of hydrogen-containing compounds the formation of radicals was found to proceed by abstraction of hydrogen atoms. The latter are very mobile at liquid nitrogen temperatures and will be immediately removed from the cell, leaving behind the heavy immobile radicals. Later on, hydrogen atoms would either recombine to form H_2, or react with molecules, yielding new radicals and H_2 molecules, or else recombine by collision with free radicals; (*ii*) any atom abstracted from the molecule by irradiation acquires excess energy which may be sufficient for its removal from the cell.

The question of why the amount of broken bonds cannot be increased by longer exposure (*i.e.* by an increase in the dose) still remains unanswered. Even with the assumption that every pair of immediately adjacent radicals will readily recombine, irrespective of their mutual orientation, the percentage of broken bonds should amount to 5–10 and not to one-tenth or one-hundredth, as observed experimentally.

Consequently, E.S.R. studies (directly under γ- or fast electron irradiation) of the radical concentration, $[R]$, as a function of time, t, and irradiation dose, D, seem to be of great interest. To the author's knowledge, the first device of this kind was made at the Institute of Chemical Physics[2,3]. Such devices are now being used elsewhere; a very good one was constructed, for instance, in the U.S.A.[13]. Some curves for the $[R] = \mathrm{f}(D)$ dependence, obtained at the Institute of Chemical Physics in the laboratories of Voevodsky and Buben, and also by some other investigators, are shown in *Figures 1* and *2*. It will be seen that the concentration of free radicals increases linearly at first with the dose, then the increase slows down and a limiting value is attained which does not change with further increase in the dose. The limiting concentrations for various substances are within 10^{18} to 10^{20} particles/$\mathrm{cm.}^3$

The question arises as to what mechanism accounts for the attainment of the limiting concentration. First of all it will be noted that when irradiation is discontinued at temperatures lower than those corresponding to the limiting value, the radical concentration will remain practically unchanged for any length of time, provided the temperature is sufficiently low. Moreover, when the limiting concentration value is not too high, there will be no drop in concentration after the end of irradiation in the saturation region as well.

This means that the saturation effect cannot be accounted for by trivial recombination of radicals, due to their diffusion in the matrix lattice. Talrose and Vassiliev of the Institute of Chemical Physics investigated a number of model mechanisms accounting for the disappearance of radicals due to various modes of motion. One obvious idea would be that when the appearance of free radicals is due to abstraction of mobile hydrogen atoms, these atoms will meet in diffusing, heavy, immobile radicals and recombine with the latter. Mathematical treatment of this suggestion gives a proportionality of radical concentrations: $[R] \propto t^{\frac{1}{3}}$. Thus, although it shows strong deviations from the linear dependence, the above suggestion does not provide an explanation for the occurrence of the limiting concentration. Moreover,

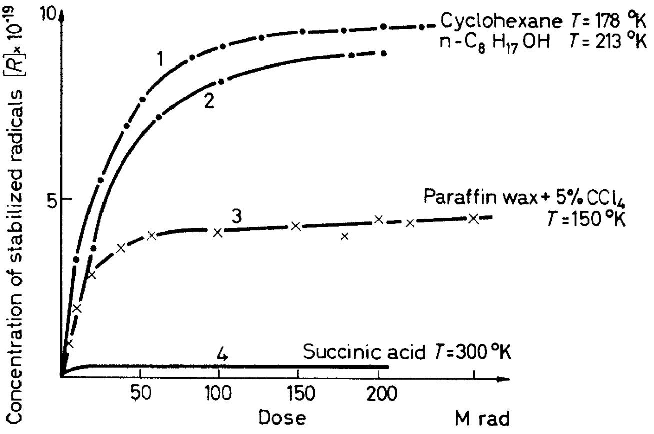
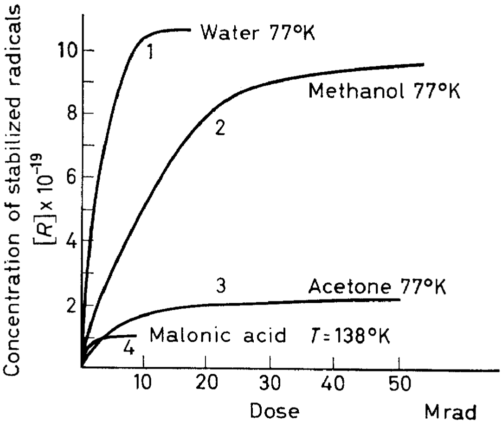


Figure 1



Figures 1 and 2. Free radical accumulation curves for solid phase irradiation

it is refuted by direct experiment, as the hydrogen atom concentration appears to be incomparably lower than would be expected from the suggestion.

Another mode of motion that could lead, in principle, to retardation of the accumulation of free radicals, is that of excitons generated by irradiation. The hypothesis based on this suggestion is that a moving exciton would be more likely to cause dissociation in the part of the molecule immediately adjacent to the free valence, resulting in a higher probability of recombination of the freshly formed radicals. Similar mechanisms dependent on migration of electrons or holes, and involving radicals acting as traps for electrons due to their high electron affinities, and for holes due to the low ionization potentials of radicals, are also conceivable[4]. However, all these mechanisms lead to proportionality in free radical concentrations $[R] \propto t^{\frac{1}{3}}$ or $[R] \propto t^{\frac{1}{2}}$, and thus provide no explanation for the limiting concentration phenomenon.

In investigating the accumulation of stabilized nitrogen atoms at liquid helium temperatures, Jackson[14] in America suggested a very ingenious model based on the assumption that stabilized atoms cease to accumulate as a result of a chain-thermal process. A special chain development of the recombination process will occur, due to the propagation of a thermal wave from the site of a random atom pair recombination to locations of other atom pairs. When the temperature in the wave reaching the other atom pairs is sufficient to bring them together and, consequently, to cause

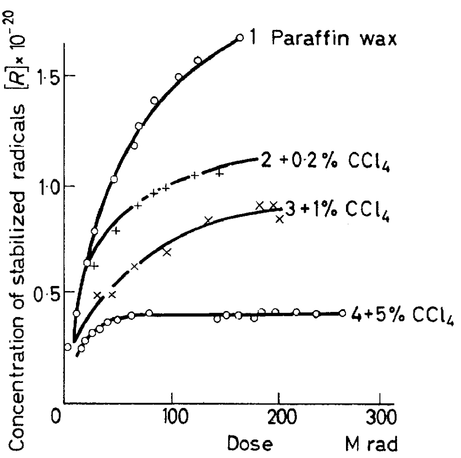


Figure 3. Curve for accumulation of radicals in paraffin wax, in the presence of CCl_4, irradiation temperature 150°K

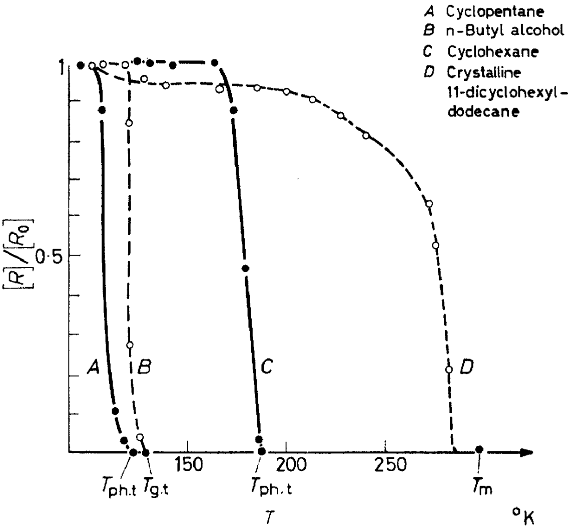


Figure 4. Curves for recombination of stabilized radicals heated after irradiation

their recombination, new sources of thermal waves will be created, and so on. Such a self-accelerated process of radical disappearance may be shown to occur only at radical concentrations above some critical value. Talrose and Vassiliev worked out a certain modification of this model, allowing for the kinetics of reactions in the thermal wave and taking into consideration the idea suggested by Lazurkin and Mokulskii[15]—that hot spikes are generated in a solid by irradiation*. It appears, however, that although the thermal model gives feasible values for the limiting concentrations for molecular crystals of diatomic gases at liquid helium temperatures, it furnishes no quantitative explanation for the limiting concentrations that occur in organic substances, in particular in polymers at liquid nitrogen temperatures and above.

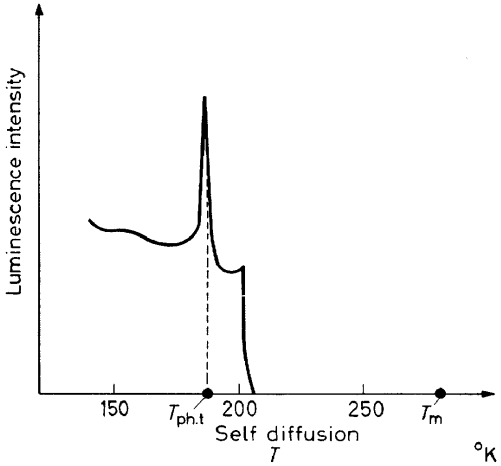


Figure 5. Radiothermoluminescence curve for irradiated solid crystalline cyclohexane; dose 30 Mrad

Finally, I think that a possible reason for the limiting concentration effect might be the crystal lattice destruction at high doses, due to radiolysis. However, the lattice destruction is not sufficient to explain the cessation of radical accumulation at very low doses, or when the concentration is greatly affected by small amounts of additives which decrease the limiting value by a factor of 1·5 to 4 (as, for instance, the addition of 0·2 to 5 per cent of CCl_4 to paraffin wax[15a]) (*Figure 3*). Thus, the whole problem of the " limiting concentration effect " still awaits theoretical solution.

Systematic studies of radical recombinations in solids after irradiation are being carried out at the Institute of Chemical Physics and at the Chemical Kinetics Department of the Moscow State University.

The main result of all investigations on radical recombination in solids is the knowledge that this recombination is directly related to phase transitions. Curves for changes in radical concentrations with gradual increase in temperature, plotted from the results of Ermolaev, Molin and Buben[156] for

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* Karpov in the U.S.S.R. showed by direct experiment[5] that diffusion in solids is greatly accelerated during irradiation.

amorphous n-butyl alcohol, crystalline cyclohexane, crystalline 1,1-dicyclohexyldodecane and crystalline cyclopentane, are shown in *Figure 4*. These substances are taken as examples because each of them displays another mode of phase transition, involving fast radical recombinations. For crystalline 1,1-dicyclohexyldodecane, phase transition occurs at the melting point, for cyclohexane at the point of polymorphous conversion, for cyclopentane at the onset of rotation in the lattice, and for amorphous n-butyl alcohol at the glass-transition temperature. It may be seen, indeed, that a sharp drop in radical concentration tending to zero corresponds to each of these phase transitions, while heating before transition causes no changes in concentration over many tens of degrees. The rate of heating for all these cases, and also for those discussed later, was 0·3 to 1°/min.

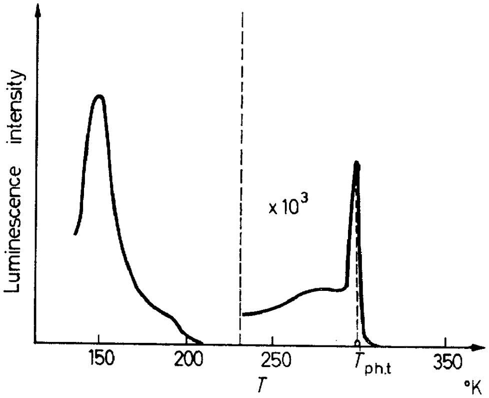

Figure 6. Radiothermoluminescence curve for Teflon: Dose 3 Mrad; the maximum at 150°K is associated with acquisition of mobility in the amorphous phase

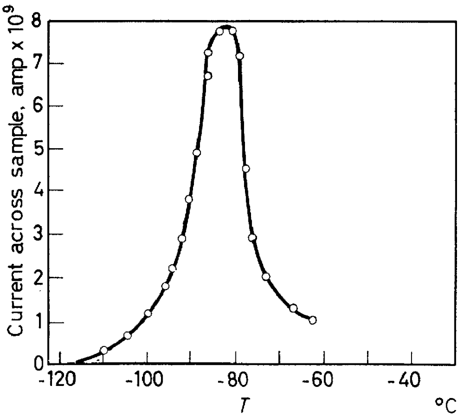

Figure 7. Electroconductivity glowing induced by heating irradiated solid heptane; maximum at the melting point

A number of other interesting physical phenomena appear to occur at the points of phase transitions in irradiated samples, such as luminescence glows observed by Nikolskii and Buben[16], and electroconductivity maxima discovered by Talrose and Frankevich[17]. These are illustrated in *Figures 5* and *6* (luminescence glows in irradiated crystalline cyclohexane) and in *Figure 7* (electroconductivity glow at the melting point of irradiated heptane). Luminescence glows accompany phase transitions and may be accepted as a new means of recording them. It must be emphasized that luminescence is, as a rule, accounted for, not by elementary processes of radical recombination, but by recombination of electrons and holes trapped during irradiation.

Table 1

Substance	*Phase transitions* (°K)	*Thermo-luminescence maxima* (°K)	*Disappearance of radicals* (°K)
Methyl alcohol (crystalline)	157, onset of rotation of the molecule 176, melting	Yet undetermined	155–175
Benzene (crystalline)	110, onset of rotation of the molecule 278, melting	133 193 228, strong maximum	228
n-Octyl alcohol (crystalline)	256, melting	Yet undetermined	256
1,1-Dicyclohexyl-dodecane (crystalline)	300, melting	137 300	300
Cyclohexane (crystalline)	135–183, onset of rotation of the molecule 186, crystal lattice rearrangement 218, onset of self-diffusion 280, melting	158 186 202	186
Cyclopentane (crystalline)	122, onset of rotation of the molecule 179, melting		122
Neopentane (crystalline)	140, heat capacity jump (supposedly lattice rearrangement from tetragonal to cubic form) 200, self-diffusion 257, melting		140
Acetone (crystalline)	178·5	110	80–100 153
Ammonium nitrate (crystalline)	257, transition from tetragonal to rhombic form 305, from rhombic to monoclinic 356, from monoclinic to tetragonal 399, from tetragonal to cubic 443, melting		250

Table 1—continued

Substance	*Phase transitions* (°K)	*Thermo-luminescence maxima* (°K)	*Disappearance of radicals* (°K)
Hydrogen sulphide (crystalline)	104, onset of rotation of the molecule 188, melting		104
25 per cent solution of hydrogen peroxide in water (crystalline)	220, melting of the eutectic mixture		220
25 per cent solution of hydrogen peroxide in water (amorphous)	158, crystallization from the glass-like state		158
n-Butyl alcohol (amorphous)	120–130, glass transition 193, melting	123	125
Glycerine (amorphous)	200–220, glass transition 292, melting	Yet undetermined	215
1,1-Dicyclohexyl-dodecane (amorphous)	190, glass transition 300, melting	123 197	190
Hexamethylbenzene	108, heat capacity jump 135–165, reorientation around a 6th order axis 384, rearrangement of the crystal lattice 439, melting	120 220	160–200 (concentration drop) 390 (disappearance)
High pressure polyethylene (amorphous–crystalline)	153 228–250, glass transitions	153 230–250	240–280 360
Paraffin wax (commercial) (amorphous–crystalline)	152 220–240, glass transitions 333, melting	152 223 330	250–280
SKB* rubber (sodium butadiene, amorphous)	227, glass transition	148 224	225
SKD* rubber (butadiene rubber without side-groups, amorphous)	176	148 178	175
Teflon (polytetra-fluorethylene)	168 295, phase transition of first order	150 295	Disappearance by the bi-molecular law

* Soviet made.

The points and temperature ranges corresponding to radical recombination and, according to Nikolskii and Buben, to luminescence glows, are summarized in *Table 1.* Various data published on phase transition points for all substances studied, and, where known, the nature of phase transitions, are also shown. It may be seen from the twenty-one examples studied that for six amorphous substances recombination takes place at glass-transition temperatures, for thirteen crystalline bodies recombination occurs in three cases at the melting points, in two—at the onset of rotation, and in five—at the point of transition of one crystal form to the other. In the remaining cases the nature of phase transition is either complex or, as yet, undetermined. In many cases heating of the system leads to a number of phase transitions that proceed without recombination, until there occurs a transition involving the recombination of practically all radicals. Cases were observed (for instance, with polyethylene) when one kind of radical disappeared by one mode of transition, and the other by another.

The recombination in amorphous bodies at glass-transition temperatures, and in crystalline bodies at melting points, is perfectly natural, as a marked increase in the mobility of all particles takes place at these temperatures. However, the reason why the onset of rotation should lead to recombination of radicals is less obvious. Recombination at the moment of lattice rearrangement can be understood, as the latter causes intensive motion within the lattice. It is more difficult to understand why irradiation of the one of two crystal forms which corresponds to a higher temperature does not lead to accumulation of radicals, as shown by experiments with ammonium nitrate, hexamethylbenzene and neopentane, carried out by Buben and Shamshev at the Institute of Chemical Physics. The reason may possibly lie in the fact that with high-temperature crystal forms certain motion is pre-liberated. It will be noted, however, that in accordance with nuclear magnetic resonance data, self-diffusion in neopentane and cyclohexane develops considerably later than the disappearance of radicals by lattice rearrangement. Much more extensive nuclear magnetic resonance studies would be necessary to elucidate this problem. Finally, transition from one crystalline modification to another may result in the appearance of multiple ultramicroscopic fissures. Diffusion of radicals along these fissures would be more rapid, thus preventing their accumulation in measurable quantities. Things are different when the substance crystallizes after the glass-transition phase. The radicals, after having disappeared at the glass-transition point, might then accumulate again in the crystalline state. This is the case, for instance, with a frozen hydrogen peroxide/water solution[6]. Radicals may accumulate here on ultra-violet illumination at temperatures below that of glass-transition (158°K); then, by increasing the temperature, radicals may be made to recombine at this point and to accumulate again on irradiation at a higher temperature. They then disappear only at the melting point of the eutectic mixture (220°K).

For samples irradiated with high doses, at which concentrations are already saturated, recombination of radicals by heating proceeds in another way. A considerable extension of the temperature range involving radical recombination, and a shift in the range towards lower temperatures, is characteristic of this change. It may be illustrated by curves for radical recombination in n-octyl alcohol[17a], irradiated with various doses (*Figure 8*). At an increase in the dose from 10 to 540 Mrad the point corresponding to completion of recombination will be shifted by some 30°, and there will be almost no horizontal part in the recombination curve. We suggest that for crystalline bodies these phenomena are connected with destruction of the crystal lattice by irradiation, and with increased mobility in the destroyed part. This is corroborated by considerable extension of the thermoluminescence region towards lower temperatures, as compared with low-dose irradiation.

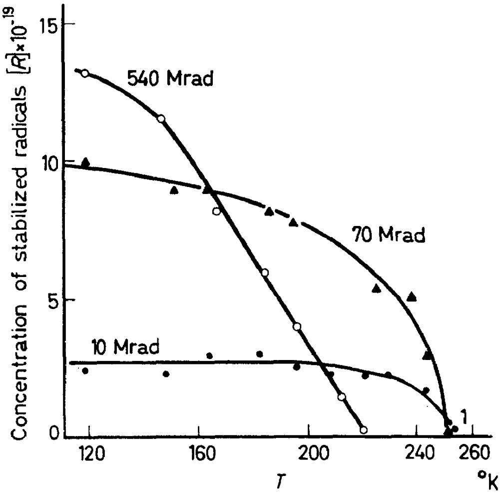

Figure 8. Curves for recombination of stabilized radicals in n-octyl alcohol at various irradiation doses; irradiation temperature 118°K, m.p. 256°K

With glass-like substances a corresponding shift in the glass-transition range is often accounted for by plastification with low molecular products of radiolysis. It follows from data obtained at the Institute of Chemical Physics that the most important part is played by accumulation of molecular hydrogen; the amounts of this hydrogen diluent may be very high and may cause a shift of several degrees towards lower values in the glass-transition temperature.

It will be noted also that the accumulation of sufficiently high concentrations of stabilized radicals would in itself produce a considerable lattice rearrangement and decrease the transition temperature.

It is of interest to note, too, that the kinetic curves for radical disappearance, *i.e.* of the curves for concentrations as a function of time at the given temperature, present a very peculiar appearance for many strongly irradiated substances. It seems that a moderate, step-wise increase in temperature of such a sample would cause a rapid drop in radical concentration; however, this drop would take place only up to a certain degree of conversion; the latter would increase with the extent of the temperature jump. After this, the concentration practically ceases to drop. A further increase in temperature would lead to another drop in the free radical concentration, which would again be discontinued later on. Thus, a whole set of true kinetic curves may be obtained with a step-wise increase in temperature, and the end part of each curve will be horizontal. The step-like curves for strongly irradiated n-octyl alcohol, and also for a 25 per cent solution of hydrogen peroxide in water[6] are shown in *Figures 9* and *10*. In the light of what has been said about non-uniform lattice destruction, this picture seems to be quite natural. It is accounted for by a sufficient number of sites differing appreciably in the activation energy for diffusion. It will be noted that with " poor " crystalline structures, similar kinetics of recombination are sometimes observed at low irradiation doses, possibly due to defects of various kinds.

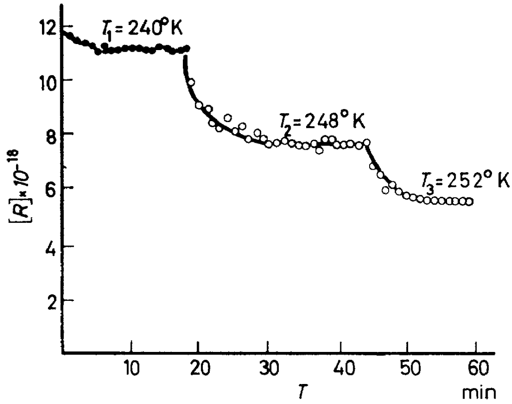

Figure 9. Kinetic curves for free radical recombinations in solid n-octyl alcohol during high-dose irradiation (540 Mrad) at stepwise temperature increase

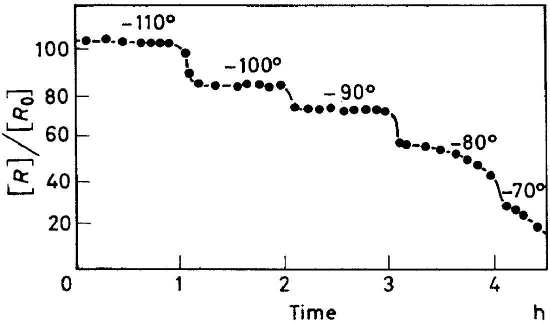

Figure 10. Kinetic curves for free radicals stabilized in a solid 25 per cent solution of hydrogen peroxide in water at stepwise temperature increase; irradiation with ultra-violet

The importance of the lattice rigidity for the recombination process is emphasized by the fact that with the same radicals in a more rigid lattice of a considerably higher phase transition temperature, the temperature of radical disappearance will also be considerably higher. For instance, Buben and Boyarchuk[7] found that in a rigid ion lattice of $MgCl_2.6CH_3OH$, the CH_2OH radicals will be stable up to 240°K, while in the considerably less rigid methyl alcohol they recombine at temperatures as low as 160°K.

ADDITION REACTIONS

After radical recombination the most simple solid phase reactions are those of addition, as they involve only minor atom displacements and are somewhat reminiscent of phase rearrangements. The second part of this paper will be concerned with addition reactions. One of the most important reactions of this kind is that of polymerization. It is more convenient to study polymerization in solids under γ- or fast electron irradiation.

To gain a better understanding of the specificity and the various features of solid phase polymerization it was necessary to investigate a number of different monomers, both in the solid and in the liquid state, under the same experimental conditions and using the same methods. The lack of such systematic work is one of the reasons for discrepancies in publications, and greatly hinders any generalization.

During the last six months, Enikolopyan's and Goldanskii's[9] laboratories have undertaken systematic investigations, using a cascade 1·6 MeV accelerator from the Institute of Chemical Physics. Irradiation of solid or liquid monomers was conducted in a thermostat ensuring a constant temperature during irradiation to within $\pm$ 2°. The doses used were from 0·5 to 10 Mrad (those for formaldehyde were considerably lower), the exposure time was from several minutes to an hour, and the polymer yields were from fractions of 1 per cent to 15 per cent. The samples were heated after irradiation and the polymer yield was determined by weight of the non-volatile residue. The monomer was completely removed by evacuation within 5 to 10 minutes. It was found that the use of inhibitors did not appreciably affect the yield. When a sample was irradiated in the solid state, then melted and kept liquid for 3 hours without evacuation, the yield was found to increase considerably, apparently because of the liquid phase post-effect. In the solid phase the post-effect seemed to be negligible, as the yield was unchanged in a sample maintained at the temperature of the experiment for 4–5 hours after irradiation.

It should be noted that this work is still in its initial stage, and that investigations are far from being complete, both with respect to the number of reactions investigated and the amount of experimental points on the initial rate to temperature curves. But the results obtained are so convincing that I shall still attempt to discuss them here in a preliminary way.

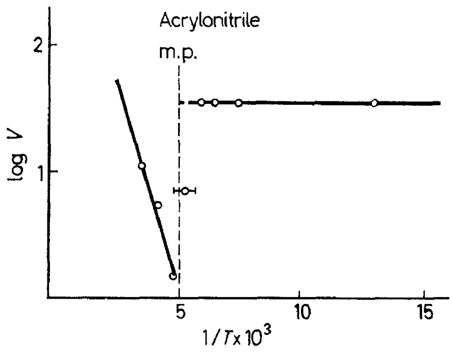

Figure 11. Temperature dependence of polymerization rate for acrylonitrile

Results of experiments with acrylonitrile (T°_{melt} — 82°) are shown in *Figure 11.* The absolute temperature reciprocal is plotted along the abscissa, and the logarithmic yield for the given dose at the initial reaction stage, *i.e.* the logarithm of the initial reaction rate, along the ordinate. For the liquid phase the rate can be seen to drop rapidly with increase in inverse temperature. At the melting point, on transition to the solid phase, the yield builds up by a factor of about 25, and farther on remains unchanged up to the liquid nitrogen temperature. In other words, the activation energy (E_{liq}) is about 3 kcal/mole for the liquid, and that for the solid phase (E_{sol}) is about 0. The degree of persistence of the steady rate in the solid phase at various temperatures and low doses is seen from *Figure 12.* The yield is plotted against the dose or, in other words, against the given intensity. The initial linear parts of the curves are seen to be practically the same for four temperatures: -107, -120, -140, $-196°$. Limiting concentration values increase with increasing temperature.

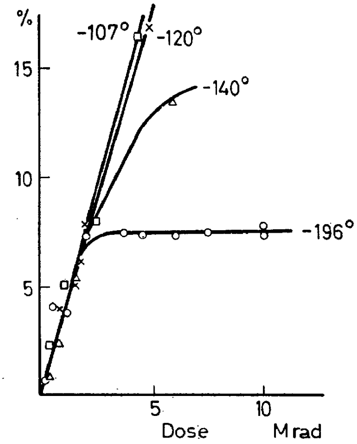

Figure 12. Acrylonitrile (solid state), kinetic curve yield of polymer-dose for temperature of:
○ — 196°
△ — 140°
× — 120°
□ — 107°

Results obtained for formaldehyde (T°_{melt} — 119°) are shown on the left-hand side of *Figure 13.* Circles correspond to Magat's results[18], and crosses to results obtained at the Institute of Chemical Physics. The yield at the melting point, on transition to the solid phase, increases about sevenfold. The activation energies, E_{liq} and E_{sol} are 2·3 and 0, respectively.

For vinyl acetate (T°_{melt} — 100°) and methyl methacrylate (T°_{melt} — 48°) $E_{\text{liq}} \simeq 3{\cdot}2$ and $E_{\text{sol}} \simeq 0$ (*Figure 13,* right-hand side); the yield at the melting point, on transition to the solid phase, remains unchanged (vinyl acetate) or even decreases about eightfold (methyl methacrylate).

Thus, at a liquid–solid phase transition the yield may either increase or decrease or remain unchanged, but the constancy of the solid phase yield over a wide temperature range, from $-196°$ to the melting point is very striking. As mentioned before, relatively low radiation doses, corresponding to initial reaction stages, were used in these experiments. With increase in dose, when the liquid phase reaction rate still remained unchanged, *i.e.* when the yield built up linearly with the dose, a gradual decrease in rate

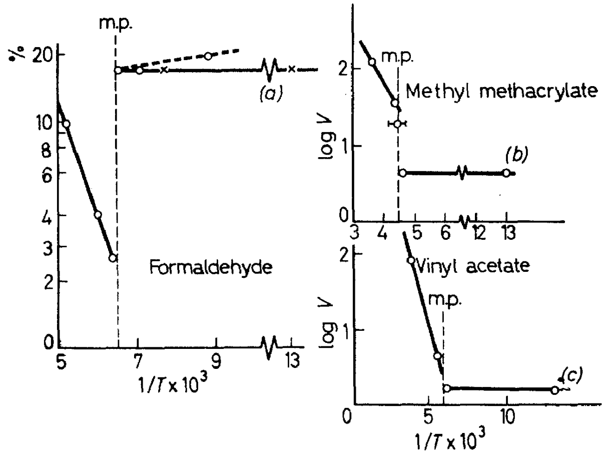

Figure 13. Temperature dependence of rate polymerization for:
(*a*) formaldehyde
(*b*) methyl methacrylate
(*c*) vinyl acetate

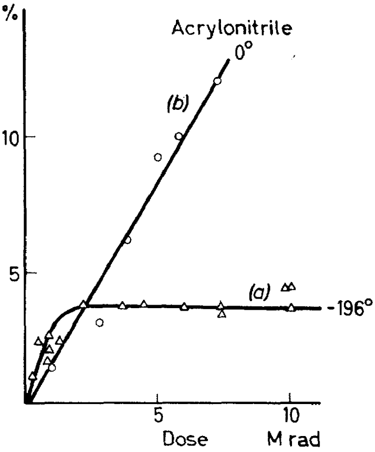

Figure 14. Kinetic curves of acrylonitrile polymerization:
(*a*) solid state (− 196°)
(*b*) liquid state (0°)

tending to zero was observed for the solid phase, *i.e.* the " limiting concentration effect " was observed at a conversion of several per cent. The kinetic curves for yield *versus* dose for acrylonitrile at − 196° (solid phase) and 0° (liquid) are shown in *Figure 14.*

It follows that true results would be obtained by comparison of initial rates only, *i.e.* at relatively low doses. At high doses, when the limiting concentration effect is already present in the solid phase, the liquid phase yields will always be higher than those in the solid.

The limiting concentration effect should always be allowed for, as it occurs at different doses for various temperatures and this may lead to an apparent temperature coefficient in the solid phase. This may be the reason for discrepancies in experimental results for the liquid and solid phase rates, and also for different temperature dependences of yields, reported by various authors.

Other regularities were observed in Enikolopyan's investigations on the radiation-induced polymerization of isobutene (*Figure 15*, upper right-hand side). A more marked confirmation of these regularities was obtained in the works of the American scientists, Lawton *et al.*[19] and Burlant *et al.*[20], on radiation-induced polymerization of hexamethylcyclosiloxane (*Figure 15*, left-hand side). Though there is a considerable spread of points, the general nature of the temperature dependence of the yield is perfectly clear. It may be seen that there is virtually no polymerization in the liquid phase, and that a considerable acceleration of the process only starts at about 8° above the melting point. For the solid phase, starting from about 40° and down to −196°, the yield remains practically constant, and a rise in the reaction rate, at first slow and then rapidly increasing, is observed only in the vicinity of the melting point, over a range of about 20°.

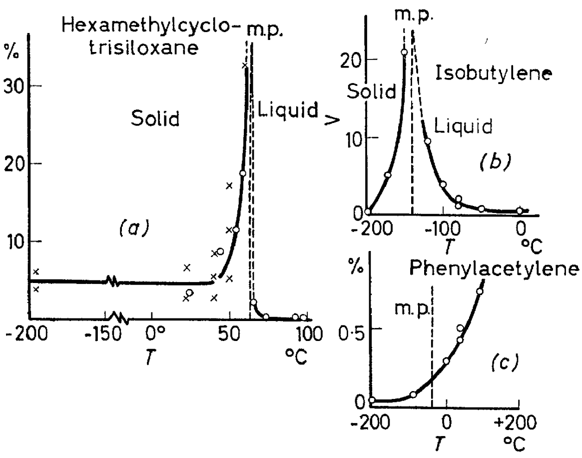

Figure 15. Temperature dependence of rate of polymerization for:
(*a*) hexamethylcyclotrisiloxane
(*b*) isobutylene
(*c*) phenylacetylene

Professor Magat has kindly informed me that similar results were obtained by Japanese investigators for radiation polymerization of some other solid monomers close to the melting point. These results are not published but were discussed at a conference in Paris.

A similar, though considerably more indefinite, picture was observed for isobutene. Finally, a case was recorded by Goldanskii, Barkalov *et al.*, when the liquid-to-solid phase transition did not affect polymerization at all. This took place with phenyl acetylene (T°_{melt} $-40°$, *Figure 15*, bottom right-hand side[8]). However, as this case is atypical, it will be disregarded here, and other observations will be discussed.

The complete independence of the reaction rate upon temperature in four of the six cases cited is especially striking. As this behaviour is at complete variance with all accepted concepts concerning polymerization, some particular reasons for this must be sought. One explanation is that there may be no reaction at all during irradiation. The latter may lead only to the formation of stabilized radicals or ions, which would initiate chain polymerization only when melting sets in. This suggestion would also throw light upon the puzzling occurrence of the limiting polymer yield in solid phase polymerization at higher radiation doses. Indeed, free radicals are known to accumulate during solid phase irradiation up to a certain limiting concentration only. The limiting polymer yield would have a simple explanation on the assumption that polymerization proceeds during melting, as the results of radicals and ions accumulated during irradiation.

If this suggestion is correct, then the true rate of radiation-induced polymerization at the melting point would be very high, while in the solid phase it would be very low.

Is there some direct evidence in support of the suggested reason for the enormous rate of polymerization at the melting point? Yes, there is. It has long been known from the results of Letort[21,22], Hinshelwood[23] and Norrish[24] that the polymerization of acetaldehyde (T°_{melt} $-123°$), for example, is very violent in the upper layer of melting crystals; its rate amounts to that of melting, while in the liquid phase (only two degrees above the melting point), or in solids, the reaction does not take place at all (this was observed by using optical methods). Something of the same kind was observed for polymerization of butyraldehyde as well[25,26].

These are, indeed, remarkable facts which cannot be explained in the light of present concepts about the mechanism of polymerization. Their importance for the elucidation of solid phase reaction mechanisms may be compared to the part played by the hydrogen–chlorine reaction, or the oxidation of phosphorus vapour, in treating the kinetics of gas phase reactions.

Enikolopyan of the Institute of Chemical Physics showed some time ago that polymerization of formaldehyde in the presence of traces of amine is also considerably more violent at the melting point, the yield amounting to 50 per cent, while slightly below the melting point, in the solid phase, the reaction is far from being violent. In the liquid phase, close to the melting point, reaction does occur, but its rate is relatively low. Kargin and his co-workers report that enormous polymerization rates at the melting point are also observed for certain monomers of the vinyl series[27–30], such as styrene, α-methylstyrene and isoprene. These investigators used the method of simultaneous condensation of the catalyst and monomer, supplied as intersected molecular beams directed on cooled surfaces, with subsequent heating. This method ensured molecular dispersion of the catalyst in the monomer. In this way, Kargin succeeded in showing that in a number of cases polymerization will be violent also at temperatures considerably lower than the melting point, namely, at points of phase transitions, for example, at the glass-transition point. Acrylonitrile, methyl acrylate, methyl methacrylate, acrylamide and methacrylamide are among the monomers whose polymerization in the solid phase, at phase transitions points, in the presence of finely dispersed catalysts, proceeds at an enormous rate[28].

Thus, direct evidence for violent catalytic polymerization at the melting point or phase transition points was obtained for the majority of monomers investigated at the Institute of Chemical Physics. It is hardly conceivable that free radicals, ions, and trapped electrons and holes, obtained by irradiation of a solid polymer, fail to act in the same way as catalysts introduced from the outside. The above-mentioned temperature dependence of the rate of radiation-induced hexamethylcyclosiloxane polymerization, with a lower maximum decreasing more smoothly towards both low and high temperatures, provides confirmation for this radiation effect. This permitted observation of the temperature dependence of the reaction in the solid phase, close to the melting point, which was impossible in the cases treated above. As stated earlier, something of this kind was also observed for isobutene.

Many scientists have probably been concerned with the question of whether polymerization might proceed as a result of melting alone. It was raised, for instance, by Magat[31]. He, however, came to the conclusion that this is not the case, and that reactions proceed in the solid during irradiation. Yet this is not consistent with the results obtained in Magat's laboratory by Bensanson and Marx[32]. They irradiated a solid monomer with a fixed high radiation dose, D, continuously in one experiment and in several stages in another, heating and refreezing the sample after each stage. A considerably higher polymer yield was obtained when using the " intermittent technique ". A similar effect was observed for acrylonitrile, the limiting concentration yield for which was mentioned above. These results seem to be convincing evidence that the reaction develops during melting.

Nevertheless, the question as to whether polymerization proceeds or not in the solid phase is not clear. It might, however, have been settled by a simple experiment, *i.e.* by thermographic analysis of a heating-up curve for a monomer irradiated at a low temperature. Unfortunately, these experiments are still only under preparation, and there was no time to obtain results before this Congress.

It will be noted that the data discussed above are similar in part to those mentioned by Professor Magat in his paper, p. 487. His results seem, to some extent, to support the concept that the reaction proceeds in the solid phase during irradiation.

In any case, we arrive at the following dilemma:

(*i*) If it transpires that the reaction does not proceed in the solid phase and is violent only at the points of melting or glass-transition, two questions will have to be answered:

(*a*) Why is the rate of radiation-induced polymerization considerably less in the solid phase than in the liquid phase?

(*b*) Why does the reaction rate become enormous at the melting or glass-transition points?

(*ii*) If it transpires that the polymer yields observed are obtained in the solid phase, immediately under irradiation at low temperatures, it would be necessary to find an explanation for the absence of temperature dependence in the solid phase, and also, for the enormous rate of catalytic polymerization at phase transition points. In seeking possible explanations I was amazed to find that the same hypothesis may be valid for both variants, depending upon the value of one parameter, which is difficult to establish and which may be different for different substances. Thus, the possibility of meeting one or the other variant in various systems is not excluded.

For the liquid phase, the activation energy for every elementary reaction, in particular for that of chain propagation, will depend upon the mutual orientation of colliding and reactive particles. Naturally, the over-all reaction rate will be determined essentially by collisions occurring within a certain solid angle, corresponding to the most favourable orientation, and the minimum activation energy, E, will be close to the over-all activation energy. The effective solid angle will apparently be above 1/100, which means that only one-hundredth of the collisions will be effective.

With a solid monomer, when there is no molecular rotation and the mutual orientation of monomer molecules in the lattice lies within the above-mentioned solid angle (let us call this " pre-orientation ") the pre-exponential factor of the chain propagation rate should be about one hundred times higher than in a liquid, while the activation energy will obviously be similar to that in the liquid phase, but sometimes higher, for reasons discussed below. Thus, the idea of " pre-orientation " suggested by many investigators, particularly Letort, cannot in itself provide an explanation for the low, and the more so for the zero activation energy, of radiation-induced polymerization in a solid monomer and the violent reactions at the melting points. However, this concept is a necessary, though not a sufficient condition for explaining the remarkable phenomena observed.

At the Polymer Symposium in Moscow last year I suggested[10,33] that practically simultaneous conversion of a large group of monomer molecules into a long polymer chain may occur in a solid monomer under the action of radiation, particularly if there is " pre-orientation ", whereas chain propagation in the liquid phase is known to involve multiple, time-separated elementary acts of addition of the monomer molecule to the growing polymer radical or ion.

After a lapse of forty years since the work of Christiansen and Kramers[34] on the probability of energy chains in gas reactions, I attempted to apply their ideas to solid phase polymerization reactions. They suggested that when a molecule is excited from outside or by thermal motion to an energy, E, the molecules of its products will possess an energy, $(E + Q)$, where Q is the heat of reaction. These hot molecules would impart by collision a portion of this energy, exceeding E, to other non-excited initial molecules and thus make them reactive. An energy chain would be propagated in this way. This concept appeared to be refuted by experimental facts and, moreover, to be theoretically impossible, as product molecules rapidly dissipate their energy by collisions unfavourable to the reaction. When E is in the form of electron excitation, it may be imparted to the molecules of the products, and then to the next initial molecule, only if the final and primary molecules have resonance levels, which is not usually the case. Thus, after almost ten years of controversy, begun in 1920, the energy chain concept gave place to the concept of substantial chains involving atoms and free radicals as active particles. However, the conditions of radiation-induced polymerization seem to favour the occurrence of energy chains. Indeed, when a monomer molecule adds to a polymer radical, the $(E + Q)$ energy will at first concentrate, at least partially, in the vibrational energy of the active end-group of the interacting radical and, if there is " pre-orientation ", the next reaction of chain propagation may be initiated before the $(E + Q)$ energy is dissipated. The formation of a long polymerization chain would be thus ensured. When E is in the form of electron excitation, this is also favourable for energy transfer in the course of chain propagation. Indeed, in an elementary reaction of a polymer radical or ion with the adjacent monomer molecule, the initial particle and the reaction products possess similar end-groups. Consequently, the electron levels of these particles will be identical and this makes possible the resonance transfer of electron excitation. Thus, polymerization may be conceived as motion of the exciton along the monomer " pre-orientation ", made still more complex, due to small displacement of the end-group atoms. Displacement of the polymer–monomer boundary will proceed at a rate of the order 10^5 cm/sec. A polymer chain involving tens of thousands of monomer molecules will be formed within 10^{-9} sec, *i.e.* practically instantaneously. Chain termination will be determined by the probability of a useless dissipation of energy, and chain initiation by the rate of appearance of radiation-induced excited monomer particles.

It will be noted that the excitation energy induced in a solid by light or by ionizing radiation may migrate along the C—C bonds without dissipation over great lengths. This follows from experiments carried out by many investigators, including those of the Institute of Chemical Physics and the Institute of Petrochemical Synthesis in the U.S.S.R.[11]. Many organic compounds show relatively long-range migrations of electrons and holes as well. It may be concluded that a migration of the kind assumed in our hypothesis of energy chains in polymerization is probable, as it would be related to the exothermic nature of the chemical process which makes polymerization conditions still more favourable.

This is a rough outline of the hypothesis I propose. It provides a simple explanation for the fact that a radiation-induced reaction may proceed in a solid with a zero activation energy. Indeed, when an energy chain propagates in a solid, the excitation energy necessary for an elementary act of chain propagation is borrowed from the energy released by the preceding act and not from the energy of thermal distribution. The primary chain-initiation act is induced by irradiation and not by thermal energy. The reaction will thus be independent of temperature.

However, the question as to whether a polymer chain may be generated at all in a solid monomer is subject to an additional condition. As the polymer density is higher than that of the monomer, the average separations between monomer molecules in a crystal and monomer groups of a polymer chain should be different. Consequently, in order to form an isolated polymer chain in the mass of the monomer crystal it would be necessary to overcome the binding forces. When this is impossible, the elementary polymer chain will involve very large separations between groups and this would make it thermodynamically unstable and capable of fast decay into its monomer components. In this case, polymerization would be impossible. But even when this is not so, the activation energy for the elementary chain propagation act will appear to be elevated, as the activated complex in addition reactions is, as a rule, of smaller dimensions than the initial molecule and, consequently, the work against elastic forces of the lattice adds to the usual activation energy. However, the propagation of an energy chain would then require a larger portion of energy, and the probability of useless dissipation of energy liberated in every act and, consequently, of chain termination would be higher. This may lead to the development of polymerization being virtually impossible.

It should be noted that conditions are different at interphases of various kinds, in particular at surfaces of microfissures. The surface layer molecules may then prove to be considerably more labile than those in the mass of the solid: the reverse applies in the course of melting. The development of energy chains at defect surfaces in polymerization will, consequently, occur considerably more readily than in the mass of the intact crystal lattice of the monomer.

It will be recalled that many unimolecular (non-chain) decomposition reactions are known to occur in the solid phase only at surfaces of lattice defects, the reaction rates being still lower than in the liquid phase (by orders of magnitude).

Thus radiation-induced polymerization proceeding in a solid by the energy chain mechanism may appear to be possible or impossible, depending upon the nature of the monomer and the properties and defects of its crystal lattice. In the liquid phase, where the formation of an activated complex is not hindered, an energy chain cannot occur, owing to the absence of " pre-orientation ". The most favourable conditions for chain propagation appear to be those at the melting point. At this interphase point the solid monomer lattice persists in a very thin layer of monomer molecules, and at the same time these molecules display the properties of a liquid with respect to the formation of active complexes, while the ordered orientation inherent in crystals still remains unchanged.

Thus, the above hypothesis may provide an explanation for the enormous polymerization rate at the melting point of crystals, or at the glass-transition point of amorphous bodies. Certainly the possibility is not excluded that for some monomers this surface layer condition may not occur, so that not all monomers will necessarily display a maximum rate at the melting point.

It would be more difficult to explain the high reaction rates on transition from the glass-like to the liquid state, as the probability of " pre-orientation " in a glass-like monomer is, as yet, undefined.

The proposed hypothesis may be seen to explain all facts observed. Two possible polymerization mechanisms can be invoked on this hypothesis: (*i*) a substantial chain propagation by a mechanism involving consecutive elementary reactions between free radicals and molecules (the usual concept), and (*ii*) an energy chain capable of converting instantaneously a pre-oriented monomer into a long polymer chain (the new concept). The first mechanism would be valid for monomer solutions and liquid monomers, and the second for solid bodies, particularly during melting. This certainly does not exclude the possibility of very slow reactions (of the post-effect type) proceeding in solids by the first mechanism.

Let us now pass to the results obtained at the Moscow State University on the development of other addition reactions at low temperatures.

The photochemically induced addition of hydrogen bromide to olefins in the liquid phase is known to proceed by a chain mechanism. Bromine atoms formed under the action of light combine with olefin molecules to form the corresponding radicals. The latter, reacting in turn with hydrogen bromide, yield the corresponding bromides and new bromine atoms, after which the cycle is repeated.

Kovalev and Sergeev[34a] investigated the addition of hydrogen bromide to ethylene in a solid mixture at −196°. Ethyl bromide and dibromoethane in the proportions of 500:1 are the only reaction products. Dibromoethane can appear only as the result of combination of bromine atoms with ethylene bromide radicals and, consequently, under these conditions the latter appear to be chain carriers. It follows from the dibromoethane to ethyl bromide ratio that the chain should consist of 250 links. Direct measurements of the quantum yield showed that the chain length was above 150 links. An increase in temperature in the course of the reaction was recorded by thermographic analysis carried out by means of a differential thermocouple, one joint of which was introduced into the irradiated solid. This proves that at least a part of the photochemical conversion observed takes place at a low temperature, at −196°, and not upon heating of the solid. As may be seen from the thermographs, the reaction does not proceed for a relatively long induction period, τ, in spite of irradiation. After the lapse of τ a fairly violent chemical process sets in and is completed within several seconds. When the radiation intensity is increased, for example fifteenfold, the induction period will decrease by the same factor. In other words, a fast reaction starts after a certain radiation dose has been reached.

Light dissociates the hydrogen bromide molecule into hydrogen and bromine atoms. The hydrogen atoms combine readily, even at −196°, due to their high mobility, and yield molecular hydrogen, as was, indeed, recorded by Kovalev and Sergeev. Thus only bromine atoms, or π-complexes of bromine atoms with olefins strongly attached to their cells, will persist*. A definite concentration of bromine atoms will be obtained in the solid mixture at a given radiation dose. Thus, a fast reaction sets in at a bromine concentration above the critical value.

The following hypothesis on the nature of this phenomenon may be proposed. The strongly attached bromine atoms apparently cannot add to a neighbouring ethylene molecule at − 196° to form the radical ethylene bromide. The latter process is very rare and, consequently, will not be recorded by the thermocouple during the induction period. However, when such a reaction does take place a single reaction chain may be supposed to propagate due to point emission of heat. This is not all. The thermal wave from this chain (naturally small in volume) travels through the solid mixture,

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* Abel and Piette[35] have recently obtained an E.S.R. spectrum for the photochemical addition of hydrogen bromide to ethylene in a neopentane solution. However, this spectrum was not interpreted.

and on coming to the nearest bromine atom may enable it to initiate a new chain reaction in its turn. As the temperature of this thermal wave rapidly drops with distance, the generation of a second chain under the action of the thermal wave would be possible only if the separation between the second and the first bromine atoms were below a certain critical value.

Thus, this avalanche process of increase in the amount of chains over the whole volume will be realized only when the average separation between bromine atoms in the solid is below the above-mentioned critical value, *i.e.* if the concentration of light-induced bromine atoms attains a certain critical value during the course of illumination. It would be of great interest to verify this generalized Jackson–Talrose theory, used by Jackson to explain the limiting nitrogen atom concentrations during irradiation of solid nitrogen at liquid helium temperatures. We have seen above that this theory, though valid for helium temperatures, cannot explain the limiting concentration of radicals at liquid nitrogen temperatures, even if it is made more precise. With a chain of some hundreds of links there will always be enough heat to promote the reaction of bromine atoms with olefins. This reaction mechanism may be considered as a propagation of a direct chain which is branched by means of elementary thermal waves. This seems to be a very interesting possibility, broadening the branched-chain concept.

Lishnevsky and Sergeev[36] investigated a number of addition reactions and one substitution reaction in the dark, at low temperatures. In the liquid phase these reactions are so fast that an adequate preparation of the mixture becomes impossible. The reaction does not proceed in a solid mixture prepared by freezing out the gas mixture in a vessel immersed in liquid nitrogen.

Table 2. Thermographic results of low temperature reaction studies

System	*Component ratios*	*Fusion temperature of components* (°C)		*Critical reaction temperature* (°C)	*Product*	*Yield percentage of theoretical values*	*Constants for products*	
		1st	*2nd*				*b.p.* (°C)	n_D^{20}
Addition reactions:								
Isobutene–bromine	1:1	−140	−7	−154	1,2-Dibromo-2-methylpropane	95	59–60/36mm	1·5105
Propene–bromine	1:1	−185	−7	−125	1,2-Dibromopropane	96	54–55/36mm	1·5198
Isobutene–hydrogen chloride	1:1	−140	−112	−146	2-Chloro-2-methyl-propane	93	49/747mm	1·3869
Isobutene–hydrogen bromide	1:1	−140	−88	−137	2-Bromo-2-methyl-propane	99	71/750mm	1·4280
Isobutene–nitrogen dioxide*	1:2	−140	−9	−80				
Propene–nitrogen dioxide*	1:2	−185	−9	−60				
Nitric oxide–oxygen	2:1	−164	−218	−190	Nitrogen dioxide	100		
Nitric oxide–chlorine	2:1	−164	−102	−115	Nitrosyl chloride	99		
Substitution reaction								
Hydrogen bromide–chlorine	2:1	−88	−102	−102	Hydrogen chloride and bromine	100		

* Products of isobutene and propene nitration were not analysed. An attempt to obtain isobutene nitration products by heating a mixture frozen in layers (0·03 mole of isobutene and 0·06 mole of nitrogen dioxide) resulted in a violent explosion.

It was shown by means of gradual heating, recorded with a thermocouple, one arm of which was introduced into the solid mixture, that a fast reaction which is completed in 1 to 3 minutes sets in at a definite temperature. In five of the cases observed this critical temperature appeared to lie somewhere between the melting points of the two components, and in four cases it was slightly lower (by 4 to 14°) than the melting point of the lower-melting component.

Thus, there are reasons for believing that reactions set in at the melting point of the eutectic. The mixtures investigated, the melting points of the pure components, the critical temperatures for the onset of fast reactions and the products obtained are summarized in *Table 2.*

A number of experimental facts lead to the conclusion that π-complexes of bromine atoms and propylene are formed at $-196°$ and that their conversion into 1,2-dibromopropane occurs at the above critical temperature which corresponds to the melting point of the eutectic.

As long ago as 1926, Shalnikov and the author observed a similar explosive reaction at a certain critical temperature in a solid cadmium–sulphur mixture. The latter was prepared in high vacuum by directing two molecular beams of cadmium and sulphur onto a glass surface cooled by liquid air. Liquid eutectics would scarcely be probable in this case.

Finally, I should like to say that chemical reaction studies at reduced and very low temperatures, commenced only recently, may lead to important and novel contributions to chemistry. A parallel may be drawn from the studies of physical properties at such temperatures. These have been pursued for more than fifty years and, after making many outstanding contributions to theoretical and experimental physics, are still enriching this science with important new discoveries.

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