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CHEMICAL REACTIONS AT TEMPERATURES CLOSE TO 77°K

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I. INTRODUCTION

A new branch of chemistry, the study of chemical processes at low temperatures, close to the boiling point of liquid nitrogen, arose in recent years and has rapidly developed. Comparatively recently chemical reactions at low temperatures appeared to be unlikely. This view arose from the fact that the Arrhenius factor, which takes into account the necessity to overcome the activation barrier, increases sharply as the temperature is reduced. Furthermore, at low temperatures most substances are in the solid state where the mobility of the species is extremely low and molecular collision necessary for reaction is difficult to achieve.

Initially, the attention of chemists, who began to work at low temperatures, was drawn mainly to the problem of formation and stabilisation of radicals. Gradually the range of problems investigated widened and at present the study of the fundamental steps in the reaction of various species in the solid phase at low temperatures is one of the central problems of modern chemical kinetics. N.N.Semenov and his school and many other Soviet scientists have made a major contribution to the development of these studies.

The present review deals with certain results of studies on chemical reactions at low temperatures obtained in the Department of Chemical Kinetics at Moscow State University, directed by N.N.Semenov. In the course of these investigations the phenomenon of a spontaneous, explosive course of many chemical reactions at temperatures close to the boiling point of nitrogen and the effect of phase transitions on chemical processes were discovered, the possibility of chain reactions in the solid phase at this temperature was demonstrated, and the special role of unstable molecular complexes of the donor–acceptor type and their aggregates in low-temperature chemical reactions has been observed.

The Review consists of three principal parts. In the first section certain problems of the preparation and reactions of radicals in the solid phase are considered. The second section deals with the characteristic features of

low-temperature chain reactions — photochemical hydrobromination of certain olefins and halogeno-olefins. In the third section a wide variety of chemical reactions occurring at low temperatures are described, and the peculiarities of the mechanism of fast spontaneous chemical reactions are examined, using the halogenation of olefins as an example.

II. PREPARATION AND REACTIONS OF RADICALS AT LOW TEMPERATURES

The problems of the formation, stabilisation, and destruction of radicals at low temperatures have been discussed in many reviews and monographs [1-5]. In order to elucidate certain general features of these processes, the mechanism and characteristic features of the photolysis of frozen aqueous solutions of hydrogen peroxide have been investigated in the Department of Chemical Kinetics of Moscow State University for many years [6-10]. The data obtained permit a deeper understanding of the specific features of the photolysis and radiolysis of aqueous solutions of other substances and suggest an approach to the problem of the detailed role of structured water in biological systems.

Hydrogen peroxide was the first substance for which the special role of phase transitions and chemical reactions at low temperatures was discovered by an electron spin resonance (ESR) study of the destruction of H_3O_2 radicals [6-8]. Depending on the rate of freezing, 25% aqueous solutions of hydrogen peroxide can be obtained at 77°K in a crystalline or vitreous state. When such specimens are irradiated at 77°K with ultraviolet light from a mercury quartz lamp, ESR measurements reveal the presence of HO_2 radicals which have a characteristic asymmetric spectrum and are formed in the reactions

$$H_2O_2 + h\nu \rightarrow 2\,OH,$$
$$OH + H_2O_2 \rightarrow H_2O + HO_2.$$

In vitreous specimens the destruction of radicals does not begin until 143°K and the radicals are completely eliminated by 158°K. In 25% hydrogen peroxide solutions this is the temperature of the glass–crystal phase transition. The destruction of radicals is associated with the fact that at the instant of phase transition changes in structure, leading to considerable mobility of the molecules, usually occur. For example in hydrogen peroxide solutions in the temperature range 153–158°K the viscosity of the glass increases so much at the instant of phase transition that a thermocouple inserted into the specimen may be withdrawn [with difficulty (Ed. of Translation)].

In crystalline specimens radicals are not destroyed at 158°K. When the specimens are irradiated with ultraviolet light below the phase-transition temperature, for example at 163°K, it is again possible to obtain a considerable concentration of HO_2 radicals. On further increase in temperature, destruction of radicals in a characteristic stepwise manner was observed (Fig. 1). The data in Fig. 1 show that in the temperature range 163–183°K a definite proportion of radicals are destroyed at each discrete temperature. The radicals are completely eliminated only at 220°K at the instant of fusion of the eutectic mixture.

A similar process involving the destruction of radicals at the instant of phase transition was also observed at 103°K in the photolysis of hydrogen sulphide frozen at 77°K.[7] Subsequently studies of the role of phase transitions in radical destruction processes were developed

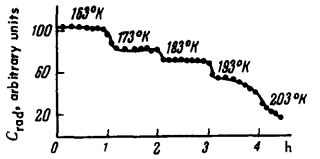


Fig. 1. Effect of temperature on the recombination of HO_2 radicals.

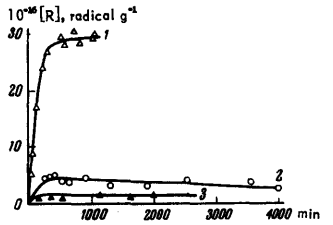


Fig. 2. Accumulation of radicals in dilute hydrogen peroxide solutions at 77°K; concentration of hydrogen peroxide (M): 1) 2×10^{-1}; 2) 4.3×10^{-2}; 3) 4.1×10^{-3}.

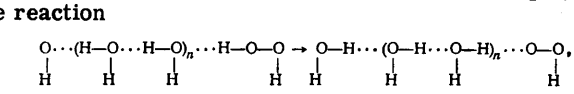
extensively in the Institute of Chemical Physics of the USSR Academy of Sciences and were summarised in Semenov's report to the Eighteenth Congress of the International Union of Theoretical and Applied Chemistry [1].

In recent years many interesting features have been observed in the photolysis of very dilute aqueous solutions of hydrogen peroxide with and without various additives. Fig. 2 shows the variation of the yield of radicals with irradiation time for various hydrogen peroxide concentrations. For the concentration 4×10^{-3} M, the ESR spectrum observed results from the superposition of the spectra of OH and HO_2 radicals. As irradiation is continued, the amount of the HO_2 admixture falls. For the solution in which the concentration is 4×10^{-2} M, the HO_2 spectrum is first observed and then the spectrum of hydroxyl radicals begins to be superimposed. The above changes in the composition of radicals are probably associated with the disappearance of the peroxide and the photolysis of HO_2 in the reaction

$$HO_2 + h\nu \rightarrow H + O_2.$$

The possibility of the photolysis at 77°K of HO_2 radicals is indicated by data obtained in a comparative study of the photolysis and radiolysis of 55% hydrogen peroxide solutions in water [9]. The concentration of HO_2 radicals during radiolysis is higher than during photolysis. When specimens subjected to preliminary irradiation from cobalt-60 were illuminated with ultraviolet light, the concentration of HO_2 radicals fell and approached the value obtained during photolysis alone. The decrease in the line-width of the ESR spectrum, which is observed on increase in the concentration of radicals, is also evidence in favour of the reaction $HO_2 + h\nu \rightarrow H + O_2$. In concentrated solutions the HO_2 radicals formed are initially distributed in pairs. With increase in the duration of illumination, part of the HO_2 radicals are photolysed and their distribution approaches statistical uniformity, which is reflected in a narrowing of the ESR spectral line.

Since diffusion of OH radicals in ice at 77°K is unlikely (OH radicals are stabilised), in order to account for the occurrence of the reaction $OH + H_2O_2 \rightarrow H_2O + HO_2$ at concentrations 10^{-3} M (55 000 H_2O molecules per H_2O_2 molecule), the hypothesis was put forward that there is a possibility of a non-diffusional bond transfer along the system of hydrogen bonds [10]. If the three-dimensional distribution of H_2O_2 molecules in a frozen dilute solution is statistically uniform and the formation of HO_2 radicals occurs in consequence of non-diffusional bond transfer, for example, by the reaction



then any significant breakdown of the structure of hydrogen bonds should result in bond transfer over much smaller distances. One would then expect that OH radicals would be stabilised at H_2O_2 concentrations in excess of 2×10^{-2} M. To check this hypothesis, we carried out experiments on the photolysis of a rapidly frozen solution of hydrogen peroxide (0.16 M) in 8 M sodium perchlorate. This solution froze into a transparent glass in which the hydrogen bond structure may be appreciably degraded. When such solutions are illuminated with ultraviolet light, the ESR spectrum of the OH radical is obtained. The initial rate of formation of radicals is smaller by a factor of approximately 100 than in the photolysis of aqueous solutions. In solutions of similar concentration but without sodium perchlorate only HO_2 radicals are observed. Thus the results of the photolysis of hydrogen peroxide in sodium perchlorate solutions appear to confirm the validity of the earlier hypothesis of non-diffusional bond transfer along the hydrogen bond system in ice.

In the photolysis of dilute aqueous hydrogen peroxide solutions the initial rate w_0 of formation of HO_2 radicals varies linearly with the concentration of hydrogen peroxide. This means that almost all the OH radicals formed in the primary step enter into the reaction $OH + H_2O_2 \rightarrow H_2O + HO_2$. However, in the photolysis of frozen hydrogen peroxide solutions to which isopropanol, which does not absorb light in the wavelength range investigated, had been added, the initial rate of formation of radicals is higher by a factor of fifty. It is difficult to explain this phenomenon. Possibly at low temperatures apart from the reactions

$$H_2O_2 + h\nu \rightarrow 2\,OH,$$

$$OH + H_2O_2 \rightarrow H_2O + HO_2,$$

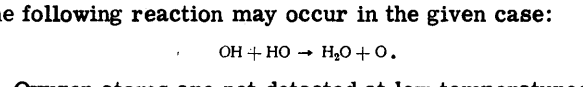
the following reaction may occur in the given case:

$$OH + HO \rightarrow H_2O + O.$$

Oxygen atoms are not detected at low temperatures by the ESR method [4]. In this case in the presence of the alcohol in the system of the two competing reactions

$$O + H_2O_2 \rightarrow OH + HO_2 \quad (\text{or } O + H_2O_2 \rightarrow O_2 + H_2O)$$

and



the second predominates, which results in an increased yield of stabilised radicals.

Another explanation of the observed peculiarities of the photolysis of dilute hydrogen peroxide solutions can be obtained on the assumption that on rapid freezing of such solutions hydrogen peroxide may be precipitated as a separate phase. Differential thermography showed that, in rapidly frozen solutions in which the hydrogen peroxide concentration is greater than 0.4 M, the peroxide is indeed evolved as a separate phase. In such a case the difference in the rate of accumulation of radicals when sodium perchlorate and the alcohol are added can probably be accounted for by the cage effect. It is a maximum for sodium perchlorate and a minimum for the alcohol. It must also be postulated that the alcohol is incorporated into the peroxide crystals.

In conclusion it must be emphasised that the study of the photolysis of very dilute frozen aqueous solutions of hydrogen peroxide in the presence of additives made it possible to elucidate a number of new interesting facts which, however, require further study. In the Department of Chemical Kinetics at Moscow State University extensive studies are being made on the photochemical and non-photochemical reactions with participation of halogens and hydrogen halides. To obtain more detailed data on the possibility of the occurrence at low temperatures of reactions of the type $X + RH \rightarrow R + HX$ (X = halogen atom) and to elucidate the characteristic features of the photolysis of binary mixtures of halogens with various organic compounds, a study was made of the formation of radicals at 77°K when mixtures of bromine and chlorine with certain hydrocarbons and alcohols are irradiated with ultraviolet light [11,12]. Compounds with weak C–H bonds and readily undergoing vitrification at low temperatures were mainly investigated. It was assumed that both these factors facilitate the formation of radicals.

The choice of alcohols was also associated with the familiar fact of the formation of molecular complexes with halogens by oxygen-containing compounds [13]. The aim was to elucidate the role of such compounds in the formation of radicals at low temperatures.

In the photolysis experiments the halogen and the organic compound were mixed in specified proportions in a vacuum apparatus. The mixture was frozen with liquid nitrogen in the tip of a quartz tube and illuminated at 77°K with filtered ultraviolet light from a PRK-7 lamp for a specified period. The specimen was then transferred to the resonator of electron spin resonance apparatus and the ESR spectra were recorded at 77°K.

After frozen mixtures of chlorine with isopentane, pentane, iso-octane, and cyclohexane had been illuminated with ultraviolet light at a wavelength $\lambda > 280$ mμm, ESR spectra revealed the presence of radicals. The experimental conditions and the results are presented in Table 1.

Fig. 3 shows as an example the ESR spectra obtained for mixtures of chlorine with isopentane and cyclohexane. The number of hyperfine structure components and their splitting in these spectra are consistent with those described in the literature [14,15] and are evidently due to alkyl radicals of the type $(CH_3)_2\dot{C}-CH_2-CH_3$ and C_6H_{11}. It should be noted that we were the first to observe at 77°K the additional splitting of each of the six components in the spectrum of the cyclohexyl radical due to β-protons lying in a plane different from the one containing the protons responsible for the main spectrum. Probably the presence of chlorine (m.p. 172°K) makes the system more rigid. The hydrocarbons used in the experiments are transparent to light at a wavelength of 280 mμm. Solid chlorine absorbs light and radicals are formed as a result of the following reactions:

$$Cl_2 + h\nu \rightarrow 2\,Cl,$$

$$Cl + RH \rightarrow HCl + R.$$

TABLE 1. Results of the photolysis of hydrocarbons in the presence of chlorine and bromine at 77°K.

Experimental conditions			Results		
halogen and its amount in mixture, moles	hydrocarbon : halogen ratio	duration of irradiation, min	state of specimen	concentration of radicals, radical g^{-1}	characteristics of ESR spectrum
Iso-octane					
Chlorine 3.9×10^{-4}	1 : 1	60	vitreous	2.1×10^{18}	11 hyperfine structure lines, $\Delta H = 13$ oersteds
Chlorine 7.4×10^{-5}	5 : 1	60	vitreous	5.0×10^{18}	ditto
Chlorine 3.9×10^{-5}	10 : 1	60	vitreous	6.7×10^{16}	
Bromine 3.9×10^{-4}	1 : 1	300	vitreous		radicals not detected
Isopentane					
Chlorine 3.9×10^{-5}	10 : 1	180	vitreous	5.6×10^{17}	8 hyperfine structure lines, $\Delta H = 24$ oersteds
Bromine 3.9×10^{-5}	10 : 1	180	vitreous		radicals not detected
Pentane					
Chlorine 3.9×10^{-5}	10 : 1	180	vitreous	3.0×10^{16}	hyperfine structure poorly resolved
Bromine 3.9×10^{-5}	10 : 1	180	vitreous		radicals not detected
Cyclohexane					
Chlorine 3.9×10^{-5}	10 : 1	180	crystalline	5.9×10^{16}	6 hyperfine structure lines with additional splitting
Bromine 3.9×10^{-5}	10 : 1	300	crystalline		radicals not detected

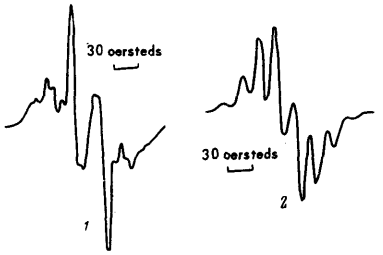


Fig. 3. ESR spectra of the radicals formed on illumination of chlorine–hydrocarbon mixtures at 77°K: 1) in cyclohexane; 2) in isopentane.

The data in Table 1 show that the yield of radicals depends on the amount of chlorine added, the number of radicals formed decreasing as the concentration of chlorine is reduced. This variation confirms the above mechanism for the formation of radicals. The yield of radicals is higher, the weaker is the C–H bond in the hydrocarbon.

It is interesting that in the photolysis of mixtures of hydrocarbons with bromine radical formation is not observed. The absence of radicals in this case is probably due to the high energy required for the reaction

$$Br + RH \rightarrow HBr + R.$$

Radical reactions with participation of bromine atoms are as a rule markedly endothermic [16], and therefore proceed with difficulty at low temperatures.

In contrast to hydrocarbons, in alcohols (methanol, ethanol, isopropanol) radicals were observed not only on addition of chlorine but also in the presence of added bromine. The mixtures were illuminated with light at a wavelength $\lambda > 280$ mμm. When the wavelength was changed from $\lambda < 280$ [sic] to $\lambda > 320$ mμm, radicals were not observed. The photolysis of alcohols with added halogens results in a complex mixture of radicals. This is because a number of secondary reactions involving the photolysis of the radicals occur during the irradiation. In their main outline these processes are similar to those observed in the photolysis of alcohols with added hydrogen peroxide. The radical reactions in methanol and ethanol during irradiation have been investigated in detail by Fok in the Department of Chemical Kinetics at Moscow State University [17,18]. In isopropanol secondary radical reactions are not observed and therefore the isopropanol–halogen system was chosen to investigate the kinetics of the accumulation of isopropanol radicals as a function of the amount of bromine or chlorine added. Experiments were made with alcohol : halogen = 10 : 1, 100 : 1, 1000 : 1, 10 000 : 1. The results obtained are presented in Table 2 and in Fig. 4.

In contrast to hydrocarbons, with alcohols there is a complex relation between the limiting yield of radicals and the amount of halogen added. The data in Fig. 4 show that the maximum yield of isopropanol radicals occurs at an alcohol : halogen ratio of 100 : 1. The initial rate of formation of radicals is also a maximum at this ratio. The occurrence of this relation and the very fact that considerable concentrations of radicals are obtained in the presence of bromine probably indicate that the mechanism of radical formation in alcohol–halogen systems is different from that in hydrocarbon–halogen mixtures.

The dissociation energies of C–H bonds in alcohols are comparable to the dissociation energies of similar bonds in branched-chain paraffins [19]. The activation energy for the reaction Br + ROH → RCHOH + HBr is about 9 kcal $mole^{-1}$

TABLE 2. Photolysis of isopropanol in the presence of added chlorine and bromine at 77°K.

Experimental conditions			Results	
halogen and its amount, moles	alcohol : halogen ratio*	duration of irradiation, min	radical concentration, radical g^{-1}	characteristics of ESR spectra
Chlorine 6.5×10^{-5}	10 : 1	720	4.5×10^{17}	in all cases the isopropanol radical was detected, with six lines at 77°K and seven lines at 110°K, $\Delta H = 21.4$ oersteds
Chlorine 6.5×10^{-6}	100 : 1	720	1.1×10^{18}	
Chlorine 6.5×10^{-7}	1000 : 1	720	5.3×10^{16}	
Chlorine 6.5×10^{-8}	10 000 : 1	720	1.4×10^{16}	
Bromine 6.5×10^{-5}	10 : 1	720	3.6×10^{16}	
Bromine 6.6×10^{-6}	100 : 1	720	7.6×10^{17}	
Bromine 6.5×10^{-7}	1000 : 1	600	6.9×10^{16}	
Bromine 6.5×10^{-8}	10 000 : 1	720	1.9×10^{16}	

* For the alcohol : halogen ratios indicated in the table, satisfactory vitreous specimens were obtained at low temperatures.

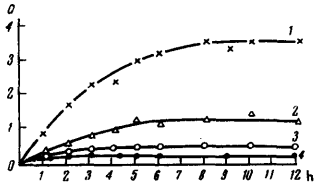


Fig. 4. Curves for the accumulation of isopropanol radicals on illumination of the bromine–isopropanol system at 77°K; alcohol : bromine ratio: 1) 100 : 1; 2) 1000 : 1; 3) 10 : 1; 4) 10 000 : 1; C is the concentration of radicals in arbitrary units.

in the case of methanol[20]. As a result of this high activation energy, direct removal of hydrogen from the alcohol molecule by a bromine atom is unlikely at low temperatures. In our view in alcohol–halogen systems radicals are formed under the action of light as a result of the condensation of the molecular charge-transfer complexes (formed during the process), which significantly alters the absorption spectrum of the system. The existence of such complexes at low temperatures is indicated by literature data. For example, Groth and Hassel established that bromine and methanol form a 2 : 1 compound which melts at 213°K.[21] X-Ray diffraction analysis showed that the alcohol molecules are linked into chains by hydrogen bonds and bromine forms cross-links between the chains.

Additional confirmation of the existence of molecular compounds in frozen mixtures of isopropanol with bromine and chlorine was obtained by the present author by a spectrophotometric method. In order to obtain the ultraviolet spectra, the halogen, alcohol, and their mixtures were frozen in the form of thin films on to a quartz plate cooled with liquid nitrogen. Fig. 5 shows as an example the absorption spectra of isopropanol, bromine, and their mixture. It is seen that, when bromine and alcohol are frozen out simultaneously, there is a marked displacement of the bromine band in the region of 384 mμm towards shorter wavelengths and a new band appears in the region of 232 mμm. Such changes in ultraviolet spectra are characteristic of charge-transfer complexes[13]. The displacement of the absorption band towards short wavelengths associated with complex formation explains the finding noted above that radicals are not formed when the wavelength of the light irradiating the mixture is changed from $\lambda > 280$ to $\lambda > 320$ mμm.

One of the possible modes of formation of isopropanol radicals consists in the excitation of the complex on absorption of light and electron transfer from the alcohol oxygen atom to bromine. Such transfer may result in the formation of the radical $CH_3-\overset{\displaystyle H}{\overset{|}{C}}-CH_3$ which under the action of light rapidly isomerises to the isopropanol radical $CH_3-\overset{\displaystyle \cdot}{\underset{\displaystyle OH}{\underset{|}{C}}}-CH_3$, whose ESR spectrum has a seven-component hyperfine structure.

The formation of molecular charge-transfer complexes is determined to a first approximation[13,19] by the ionisation potential of the donor and the electron affinity of the acceptor. Since the difference between the electron affinities of bromine and chlorine is small (1.3 and 1.2 eV)[22] and radicals are formed in alcohols as a result of the photolysis of molecular complexes, their yield should depend only slightly on the nature of the added halogen. The data in Table 2 confirm this conclusion. In contrast to alcohols, hydrocarbons do not form molecular complexes with halogens. Here the formation of radicals depends mainly on the energy relations of secondary reactions and also on the mobility of the halogen atoms, which is determined by their size and the excess energy which they receive during photolysis. The formation of radicals in mixtures of alcohols with halogens occurs in a fundamental step which consists in the photolysis of an intermediate which is stable only at low temperatures. Radicals are formed as a result of electron transfer, and the cage effect is then probably excluded. The suggested mechanism

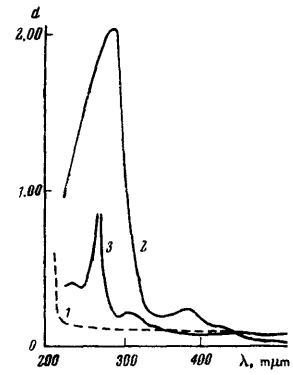


Fig. 5. Ultraviolet absorption spectra at 77°K:
1) isopropanol; 2) bromine; 3) bromine–alcohol mixture.

differs from those described in the literature for the photolysis of frozen alcohols[4,17,23]. The mechanism of radical formation by the photolysis of molecular complexes is probably common to all systems in which donor–acceptor interaction is possible.

The problem of reactions with participation of radicals during the formation of the latter is of fundamental importance both for the problem of the stabilisation and accumulation of radicals and for the possibility of carrying out various low-temperature reactions. For the solution of these problems, the author has used simultaneously electron spin resonance and gas–liquid chromatography. The results obtained in the study of the radiolysis of isopropanol will be given as an example.

The alcohol, purified from traces of acetone on a semi-preparative chromatograph, was freed from dissolved air and irradiated with X-rays for 3 h at 77°K and 90°K. The irradiated specimens were then transferred to the resonant cavity of the ESR apparatus for the determination of the concentration of the isopropanol radicals formed. After the ESR spectra had been measured, the irradiated alcohol specimens were heated to room temperature and analysed. The products were determined with a gas–liquid panchromatograph fitted with a macro-argon detector. The stationary phase was poly(ethylene glycol) with a molecular weight of 400. A large amount of acetone was detected in the reaction products. Preliminary calibration of the detector with artificial mixtures made it possible to make quantitative measurements. The results are presented in Table 3.

The isopropanol radicals obtained in the radiolysis can probably recombine on heating:

$$CH_3-\overset{\displaystyle \cdot}{\underset{\displaystyle OH}{\underset{|}{C}}}-CH_3 + CH_3-\overset{\displaystyle \cdot}{\underset{\displaystyle OH}{\underset{|}{C}}}-CH_3 \rightarrow CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle OH}{\underset{|}{C}}}-\overset{\displaystyle CH_3}{\underset{\displaystyle OH}{\underset{|}{C}}}-CH_3,$$

with formation of pinacol, and disproportionate

$$2\,CH_3-\overset{\displaystyle \cdot}{\underset{\displaystyle OH}{\underset{|}{C}}}-CH_3 \rightarrow CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-CH_3 + CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_3,$$

with formation of acetone and isopropanol. Pinacol could not be detected in the reaction products. Probably its amount is smaller than 10^{-8} g per microlitre, the minimum

TABLE 3. Amount of radicals and acetone in irradiated isopropanol.

Temperature, °K	Amount of radicals in 1 μl, g	Amount of acetone Q_T from radicals in 1 μl, g	Amount of acetone Q_A found by analysis in 1 μl, g	Difference $Q_A - Q_T$ in 1 μl, g
77	$1.1 \cdot 10^{15}$	$5.3 \cdot 10^{-8}$	$2.2 \cdot 10^{-7}$	$17 \cdot 10^{-8}$
90	$1.6 \cdot 10^{15}$	$7.7 \cdot 10^{-8}$	$2.7 \cdot 10^{-7}$	$19.3 \cdot 10^{-8}$

quantity of pinacol which could be detected in the artificial mixtures. Thus the data in Table 3 show that, when the frozen alcohol is heated, the isopropanol radicals mainly disproportionate. This is consistent with the known fact that disproportionation reactions of free radicals require a smaller activation energy than their recombination[24].

Comparison of the data in columns 3 and 4 of Table 3 shows that a large part of the acetone forms during radiolysis in the solid phase. Under the present experimental conditions the yield of radicals varies linearly with dose. Assuming that acetone forms in the solid phase as a result of radical disproportionation and that its yield follows a similar linear relation, it is possible to estimate from the data in Table 3 by the Arrhenius equation the energy of disproportionation of isopropanol radicals as 150 cal mole^{-1}. This value is consistent with the literature data for similar reactions[24] and shows that the simultaneous application of ESR and gas chromatographic methods in combination with low temperatures opens up great possibilities for quantitative investigations of fundamental reactions.

III. CHAIN REACTIONS IN THE SOLID PHASE AT TEMPERATURES CLOSE TO 77°K

Chain reactions with participation of free radicals occur widely in both gas and liquid phases[16,25]. The occurrence of such reactions at low temperatures is of considerable theoretical and practical interest. The possibility of accumulation at the boiling point of liquid nitrogen of considerable non-equilibrium concentrations of radicals and the appearance of stable products under these conditions suggested that chain reactions can also occur in the solid phase. It might have been expected that such reactions would proceed most readily upon irradiation.

We chose for investigation the photochemical hydrobromination of olefins and halogeno-olefins. In gas and liquid phases these reactions occur under the action of light and are typical chain reactions with a chain length of thousands of units[16]. It has been established that photochemical hydrobromination of olefins in the solid phase at 77° proceeds vigorously and explosively[26-28]. The products are alkyl bromides.

The experiments were made in a vacuum apparatus. A mixture of hydrogen bromide and the appropriate olefin was condensed in the reaction vessel, cooled with liquid nitrogen, and then illuminated for a specified period. The reaction was followed by differential thermal analysis. The extent of reaction was usually determined from the change in pressure after heating the irradiated mixture to room temperature. The extent of reaction increased with the duration of irradiation at 77°K. A number of special experiments established that the reaction is initiated by bromine atoms which are formed on photolysis of hydrogen bromide[26]. The formation of radicals during the preliminary illumination of mixtures of hydrogen bromide with unsaturated compounds was detected by the ESR method (in the photolysis of hydrogen bromide–cyclohexene mixtures). The resulting ESR spectrum was similar to that quoted by Abell and Piette[32].

Exact determination of the quantum yield at low temperatures in mixtures of hydrogen bromide and olefins is difficult, because the mixtures are polycrystalline and scatter light to a marked degree. In measurements involving ferric oxalate intensitometry only the number of quanta incident on an amount of mixture which virtually did not transmit light was estimated. The lower limit of the quantum yield obtained in this way for the hydrobromination of ethylene proved to be 150.

The chain length was also estimated on the basis of chromatographic data. In the gas-chromatographic analysis of the products of the low-temperature photochemical hydrobromination of ethylene[29] a considerable amount of 1,2-dibromoethane was detected in addition to ethyl bromide, the ethyl bromide : 1,2-dibromoethane ratio being 500 : 1. The presence of 1,2-dibromoethane in the reaction products shows that the reaction has a radical mechanism. If it is supposed that at low temperatures the reaction proceeds by the same mechanism as in the gas phase, 1,2-dibromoethane may form as a result of the recombination of radicals which propagate the chain hydrobromination of ethylene according to the following mechanism:

$$HBr + h\nu \rightarrow H + Br,$$
$$Br + C_2H_4 \rightarrow C_2H_4Br,$$
$$C_2H_4Br + HBr \rightarrow C_2H_5Br + Br,$$
$$C_2H_4Br + Br \rightarrow C_2H_4Br_2.$$

The chain length can be defined[16] as the number of molecules of the main product formed as a result of chain reaction per active centre. On the basis of the above mechanism, the chain length can be estimated as 250 units from the ethyl bromide : 1,2-dibromoethane ratio obtained.

Since in the determination of the quantum yield the amount of reaction products was found after heating the mixture, it is important to emphasise that the hydrobromination reactions occur in the solid phase below the melting points of the starting components. This is clearly shown in Fig. 6 in which we have plotted thermographic curves for the hydrogen bromide–ethylene system obtained when mixtures subjected to preliminary irradiation with various doses of ultraviolet light at 77°K were heated. The occurrence of reaction in the solid phase is also indicated by the considerable increase in the yield of ethyl bromide with time in an irradiated mixture. For example,

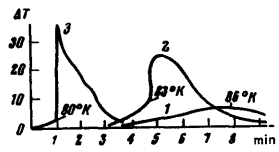


Fig. 6. Thermographic curves for equimolar mixtures of hydrogen bromide and ethylene; temperature of preliminary light irradiation 77°K:
1) light irradiation dose $D = 0.6$ (arbitrary units), extent of reaction 15%; 2) $D = 0.9$, extent of reaction 14%; 3) $D = 39.5$, extent of reaction 37%.

the extent of reaction increases by 25–30% if the mixture is kept in the dark for 1 h at 77°K before measurements. At high light intensities the reaction is explosive and may occur when actually exposed to the light beam at 77°K. The shape of the thermographic curve is then similar to that of curve *3* in Fig. 6.

An interesting feature of the hydrobromination of ethylene at 77°K is that the rapid reaction is preceded by an induction period, the explosion itself always occurring after exposure to the same radiation dose[28]. This finding is clearly shown by the data presented in Table 4. Thus the induction period τ is inversely proportional to the intensity I, while the dose $D = I\tau$ = const., i.e. the development of the explosive chain reaction at low temperatures requires the accumulation of a specified concentration of active centres, which is clearly determined by the dose and not the intensity.

Another interesting feature of the photochemical hydrobromination is its marked dependence on the conditions of heat exchange with the surrounding medium. If, for example, the heat exchange is reduced, the rapid reaction begins after smaller radiation doses, and conversely if the heat exchange is increased, there is no reaction at all at the temperature of liquid nitrogen for low radiation doses. Here reaction occurs at higher temperatures. The above features of the photochemical hydrobromination of ethylene are associated with the possibility of stabilisation of active centres and show that in low-temperature chain reactions the properties of chain and thermal explosions are closely interlinked.

At low temperatures the frozen mixtures of hydrogen bromide with olefins are polycrystalline and it was of considerable interest to elucidate which features of photochemical chain hydrobromination are characteristic of the crystalline state and which are characteristic of the vitreous state. Transparent glasses are formed when allyl chloride and its liquid mixtures with hydrogen bromide are rapidly cooled to 77°K. When such glasses are exposed to ultraviolet irradiation at 77°K and then warmed, chain hydrobromination occurs in the solid phase below the melting point of the mixture. The quantum yield of the low-temperature photochemical hydrobromination of allyl chloride is about 50. The occurrence of the reaction in the solid phase was confirmed with the aid of infrared spectra obtained in a special cuvette where the low-temperature photolysis could be carried out and the infrared spectra recorded.

TABLE 4. Dependence of the induction period τ in the hydrobromination of ethylene on the intensity of illumination (I) at 77°K*.

I/I_0	τ, s	ΔT, °K	ΔT_M, °K	η, %	D_{exp}
1	4.4	0.9	31	17.1	4.4
0.62	6.5	1.1	30	16.4	4.0
0.51	9.0	1.0	31	16.3	4.6
0.34	11.5	1.0	30	16.0	3.9
0.25	16.3	1.3	31	16.2	4.1
0.10	45.7	1.1	30	15.2	4.6
0.04	no explosion, on subsequent heating reaction occurs at higher temperatures				

* All the values in the table are averages from several experiments: ΔT is the temperature rise at the end of the induction period, ΔT_M the maximum temperature rise, η the extent of reaction, and $D_{expl} = I\tau$ the radiation dose resulting in explosion. The radiation dose is expressed in arbitrary units. The amount of radiation received by the specimen at maximum intensity I_0 from a PRK-7 lamp in 1 s was adopted as one unit.

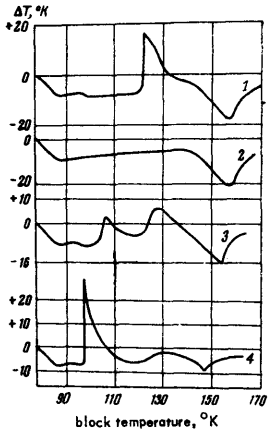


Fig. 7. Temperature variation of the difference between the specimen and block temperatures ΔT (deg) for allyl chloride and its mixtures with hydrogen bromide: 1) vitreous allyl chloride specimen; 2) crystalline specimen; 3) vitreous specimen irradiated with ultraviolet light at 77°K for 5 s; 4) similar specimen irradiated for 180 s.

Fig. 7 presents the results of a study of the hydrogen bromide–allyl chloride system by differential thermal analysis[30]. It is evident that the allyl chloride frozen to a glass crystallises at 110°K and melts at 136°K. The equimolar mixture of hydrogen bromide and allyl chloride behaves similarly.

When vitreous hydrogen bromide–allyl chloride specimens irradiated at 77°K are warmed, the thermograms (Fig. 7) reveal the occurrence of a new exothermic process at about 88°K. This process is associated with the hydrobromination since the temperature rise at 88°K is directly proportional to the amount of 3-bromo-1-chloropropane. The formation of 3-bromo-1-chloropropane as the main reaction product was confirmed by gas-chromatographic analysis. The effect of the duration of illumination on the form of the thermographic curves for the vitreous equimolar hydrogen bromide–allyl chloride mixtures is shown in Table 5.

The data in Table 5 show that the temperature of the start of reaction is independent of the duration of the preliminary illumination of the mixture at 77°K. This fact constitutes the most interesting peculiarity of the photochemical chain hydrobromination in the vitreous systems. In crystalline mixtures of allyl chloride and hydrogen bromide the temperature range in which the reaction takes place (the reaction occurs only on heating) depends on the duration of the preliminary irradiation of the mixture at 77°K. In its main outline the reaction is of the same type as in frozen mixtures of ethylene and hydrogen bromide.

The surprising finding that the temperature of the onset of reaction is independent of the duration of the preliminary

TABLE 5. Results of a thermographic study of the hydrogen bromide–allyl chloride system as a function of the time of the preliminary irradiation at 77°K*.

t	T_1	ΔT_1	T_2	ΔT_2	T_f	ΔT_f	t	T_1	ΔT_1	T_2	ΔT_2	T_f	ΔT_f
1	88	11	110	7.0	128	7.0	45	85.5	33.5	108	5.5	126	3
5	86.5	25.5	110	3.5	125	4.5	80	87.5	36		0.2	129	2
15	88	28.5	112.5	2.0	126	3	120	88	36	115	2	127	2
							240	89.5	39				

* t is the duration of irradiation (minutes) of the specimens at 77°K, T_1, T_2, and T_f are the temperatures of hydrobromination, crystallisation, and fusion respectively, ΔT_1 and ΔT_2 are the maximum temperature rises during the reaction and during crystallisation, and ΔT_f is the height of the fusion peak (°K).

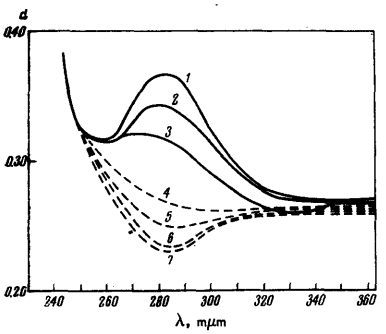


Fig. 8. Ultraviolet absorption spectra at 73°K: 1) non-irradiated mixture of hydrogen bromide and allyl chloride; 2) after irradiation with filtered light (313 mμm) for 25 min 41 s; 3) ditto after irradiation for 49 min 30 s; 4) mixture of hydrogen bromide and allyl chloride after heating to 103°K, spectrum recorded at 73°K; 5) mixture without complex after irradiation for 60 min with filtered light (313 mμm); 6) duration of irradiation 120 min; 7) duration of irradiation 180 min.

irradiation can be explained by supposing that 86–88°K constitutes the low-temperature limit of the softening of the hydrogen bromide–allyl chloride glass. In the glass-softening range there is a change[31] in properties of the system such as heat capacity, viscosity, specific volume, thermal conductivity, etc. In the given case the decrease in the viscosity of the system probably plays the main part, increasing the mobility of the reacting species and facilitating the initiation of the reaction by the active reaction centres stabilised at 77°K and produced during the preliminary irradiation. The rapid increase of the viscosity in the softening range is actually responsible for the virtually complete independence of the temperature of the onset of reaction of the dose of preliminary irradiation. The "healing" of the cracks formed in the glass at 77°K is a qualitative indication that the softening of the hydrogen bromide–allyl chloride glass occurs at temperatures below 90°K. The glass softening range was also determined thermographically from the jump in heat capacity. The thermograms of allyl chloride and of non-irradiated hydrogen bromide–allyl chloride mixtures reveal a weak endothermic process which begins at about 87°K.

The hydrobromination of olefins and halogeno-olefins occurs in systems where there is a possibility of donor–acceptor interaction which leads to the formation at low temperatures of unstable molecular compounds[33]. The role of such complexes in the formation of radicals under the action of light at low temperatures has already been mentioned in the first part of this review. Certain aspects of the participation of such complexes in low-temperature chain reactions are examined below, using the hydrogen bromide–allyl chloride system as an example[34].

Fig. 8 shows ultraviolet spectra of the hydrogen bromide–allyl chloride system. Spectrophotometric study of hydrogen bromide–allyl chloride films frozen on to a quartz plate at 80°K revealed an absorption band with a maximum at 283 mμm. When such mixtures are heated to 103°K and then cooled again to 80°K, this band vanishes irreversibly. The result shows that during condensation on to the cooled quartz plate hydrogen bromide and allyl chloride form a compound which is stable only at the temperature of liquid nitrogen.

Hydrogen bromide is an electron acceptor whereas allyl chloride can behave as an electron donor. In hydrogen bromide–propane mixtures, which were investigated at the same time, the 283 mμm band was not observed. The experimental data obtained suggest, when considered together, that the 283 mμm band of the hydrogen bromide–allyl chloride mixtures is probably due to a charge-transfer complex which forms during the condensation of the starting materials.

In a study of the effect of the amount of hydrogen bromide and allyl chloride on the intensity of the 283 mμm absorption band it was found that an increase in the concentration of either the donor or the acceptor causes a decrease in the intensity of the absorption band. The total amount of mixture was kept constant in these experiments. This type of variation of the intensity of the absorption band with mixture composition indicates that a 1 : 1 complex forms.

In order to elucidate the role of complexes in low-temperature reactions, a comparative study was made of the dependence of the extent of reaction on the duration of irradiation with filtered light (filter with a transmission maximum in the region of 313 mμm) of hydrogen bromide–allyl chloride mixtures with the absorption at 283 mμm characteristic of the complex, and mixtures in which there was no appreciable absorption in this region, the hydrogen bromide–allyl chloride system being heated to 103°K before irradiation with ultraviolet light at 77°K. As stated above, such heating breaks down the complex. Figs. 9 and 10 show the variation of the optical density at 283 mμm and of the extent of reaction with the duration of irradiation. The results obtained indicate the participation of unstable molecular compounds of hydrogen bromide and allyl chloride in the hydrobromination reaction. Data derived from thermographic analysis and infrared spectra show that the decrease of the optical density during irradiation is not associated with an appreciable occurrence of hydrobromination at 80°K. On the other hand, on raising the temperature (Fig. 10) the extent of reaction reaches almost 100%, and a high quantum yield indicates that a chain reaction takes place. Thus the data taken together suggest that at temperatures 77–80°K active centres are formed, probably mainly as a result of the photolysis of unstable molecular complexes.

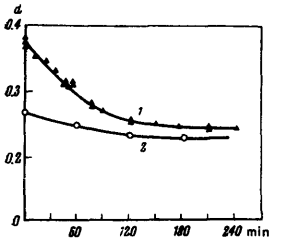


Fig. 9. Variation of optical density with the duration of irradiation in the system hydrogen bromide–allyl chloride at 73°K:
1) irradiation of mixture with complex;
2) irradiation of mixture without complex;
3) curve obtained by graphical subtraction of curve 2 from curve 1.

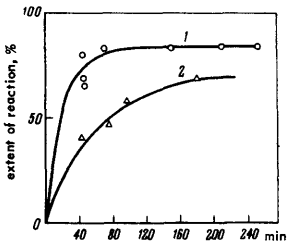


Fig. 10. Variation of the degree of reaction with the time of irradiation in the photochemical hydrobromination of allyl chloride:
1) reaction in the system with complex;
2) reaction in the system without complex.

At 77°K the active centres which initiate the hydrobromination of olefins can also form as a result of the reaction $HBr + h\nu \rightarrow H + Br$. The results obtained in a photometric study of the hydrogen bromide–allyl chloride system make it possible to estimate the contributions of various reactions to the formation of active centres. On the basis of these data, the formation of active centres under the action of light in the solid phase at 80°K can be represented thus:

$$\pi\langle^{A^n}_{C_3H_5Cl} + HBr \rightarrow H + Br'$$

where π is the complex and n the number of active centres formed from the complex.

The curves in Figs. 9 and 10 permit an approximate estimate of the relative contributions of various modes of reaction. Comparison of the yields in the initial stage of the photolysis (Fig. 10, curve *1*) and after 1.5 h when all the complex has been almost completely used up indicates the greater effectiveness of the reaction occurring with participation of the complex compared with the reaction in the system without the complex. For example, during the period of existence of the complex $\tau = 0.2t$, where t is the time of irradiation of the mixture corresponding to 85% conversion, the reaction proceeds to the extent of 62%.

On the basis of the above mechanism and using the initial condition $\pi = \pi_0(HBr) = (HBr)_0$, a system of differential equations was set up, and solved with the aid of MN-7 non-linear modelling apparatus. Analysis of the curves obtained showed that, in the initial reaction stage, the formation of active species with the participation of the complex is several times faster than the formation of active species from hydrogen bromide, although the concentration of the complex is smaller than that of hydrogen bromide approximately by a factor of ten. Thus, in contrast to gas and liquid phases, where chain initiation occurs as a result of the photolysis of hydrogen bromide, in the solid phase at low temperatures the active centres are formed mainly under the action of light from unstable intermediate compounds of the donor–acceptor type.

The development of a chain reaction in the solid phase is also affected by particular features of the chain termination reactions. Study of the dependence of the degree of hydrobromination of ethylene η on the light irradiation dose in liquid (112°K) and solid (77°K) phases showed that the degree of reaction in the solid phase is smaller for the same light irradiation dose [30]. In the liquid phase η increases linearly with dose, while in the solid phase it decreases as the dose is increased, which is probably an indication of a decrease in chain length with increase in the concentration of stabilised active centres. Chain termination in the solid phase probably occurs as a result of recombination of the active centres responsible for chain propagation with stabilised active reaction centres.

The possibility of accumulation at low temperatures of considerable concentrations of active centres exerts a significant influence also on the chain propagation reactions. In frozen hydrogen bromide–ethylene mixtures the accumulation of stabilised active centres is accompanied by a slow reaction whose rate depends on the concentration of the centres. Under certain conditions, when the rate of heat generation by the reaction exceeds the rate of heat removal from the system, a vigorous exothermic process takes place by a thermal explosion mechanism.

Semenov regarded the rapid photochemical hydrobromination of ethylene at 77°K as an unusual kind of chain explosion, in which the increase in the number of stabilised active centres entering into reaction is due to the heat of the reaction itself.

The possible mechanism of the reaction can be represented as follows. Most of the active centres formed under the action of light at 77°K are stabilised, and only in rare cases, for example on recombination of two active centres near a third centre, can an individual reaction chain of several hundreds of units arise. The occurrence of such a reaction chain is accompanied by an intense thermal wave (the hydrobromination of olefins is an exothermic reaction), which causes new, stabilised active centres to enter into the reaction. Semenov called such a mechanism the development of a straight chain which undergoes branching occurring with the aid of elementary thermal waves. Thus the results obtained in the study of low-temperature photochemical hydrobromination of olefins, together with data on low-temperature polymerisation, enabled Semenov to formulate the hypothesis of the important role of energy chains in the occurrence of chemical reactions at low temperatures.

IV. RAPID SPONTANEOUS CHEMICAL REACTIONS AT LOW TEMPERATURES

In the first two sections low-temperature reactions initiated by light were examined. This section deals with

TABLE 6. Results of a thermographic study of certain chemical reactions at low temperatures*.

System	T_f, °K component I	T_f, °K component II	T(rapid reaction), °K	Principal products	Yield, %
Chlorine–ethylene	104	172	106,119,171	1,2-dichloroethane	97
Chlorine–propene	88	172	91,111,147	1,2-dichloropropane	92
Chlorine–isobutene	133	172	112,130	1,2-dichloro-2-methylpropane	80
Chlorine–styrene	242	172			
Chlorine–thiophen	245	172			
Bromine–propene	88	266	117,158,193	1,2-dibromopropane	98
Bromine–isobutene	133	266	120,133,188	1,2-dibromo-2-methylpropane	96
HBr–isobutene	133	186	84,119,150	2-bromo-2-methylpropane	98
HCl–isobutene	133	159	100,119,133, 155	2-chloro-2-methylpropane	93
N_2O_4–propene	88	262	238	nitro-nitrate and nitroso-nitrate	
N_2O_4–isobutene	133	262	200	ditto	
N_2O_4–but-1-ene	143	262	233	»	
N_2O_4–hex-1-ene	133	262	241	»	
N_2O_4–cyclohexene	169	262	207	dinitrocyclohexane and nitro-nitrates	
N_2O_4–cyclopentadiene	188	262	183	ditto	
Nitric oxide–oxygen	109	54	88	nitrogen dioxide	100
Nitric oxide–chlorine	109	172	108,143,157	nitrosyl chloride	100
HBr–chlorine	186	172	91,168	hydrogen chloride and hydrogen bromide	100
HCl–nitrogen dioxide	159	262	193	nitrosyl chloride, chlorine, and water	97
Bromine–toluene		266	131,203	hydrogen bromide and substituted toluene	95

* The initial component ratios are 1 : 1, except for nitric oxide with oxygen and chlorine for which the ratios are 2 : 1. In the reaction temperature column the temperatures at which the main bulk of the substance reacts are underlined. Chlorine reacts with thiophen and styrene at the instant of condensation. The nitro--compounds were analysed spectroscopically.

certain peculiarities of the kinetics of a large number of various spontaneous rapid chemical reactions at very low temperatures, discovered in the Department of Chemical Kinetics. Table 6 presents part of the results obtained in a thermographic study of certain chemical reactions at low temperatures[35-38]. In order to eliminate the possibility of reaction in the gas phase at the instant of condensation, the starting materials were frozen in the reaction vessel in the form of individual layers. The technique of the thermographic investigation has been described[36,40].

It is evident from the data in Table 6 that the following reactions can take place at low temperatures: addition of halogens, hydrogen halides, and nitrogen tetroxide to double bonds; inorganic addition reactions ($NO-O_2$ and $NO-Cl_2$ systems); inorganic exchange substitution reactions ($HBr-Cl_2$ system); substitution in aromatic compounds (bromine–toluene system); inorganic redox reactions (NO_2–HCl system).

The technique involving the freezing of the initial components as individual layers prevents their coming into contact at elevated temperatures and makes it possible to verify the possibility of the spontaneous occurrence of the reactions at low temperatures. However, the mixing of the initial reactants is then so poor that the reactions must be hindered. It may be expected that in homogeneous mixtures the reactions would occur at much lower temperatures. To test this hypothesis, a study was made of certain reactions in condensates prepared by freezing out from molecular beams[41]. The molecular beam method for the study of chemical reactions at low temperatures was developed by Semenov and Shal'nikov[42]. Recently this method was successfully used to study low-temperature

TABLE 7. Low-temperature halogenation and hydrohalogenation of unsaturated compounds in mixtures prepared by the molecular beam method*.

System	T_f, °K component I	T_f, °K component II	T(rapid reaction), °K	Principal products	Yield, %
Bromine–ethylene	104	266	103	dibromoethane	93
Bromine–propene	88	266	90	1,2-dibromopropane	95
Chlorine–cyclohexene	169	172	98	dichlorocyclohexane	90
Bromine–cyclopentadiene	188	266	98		
HBr–cyclopentadiene	188	186	103		

* The reaction temperatures indicated are averages from a large number of experiments. The discrepancies are within the range of 5 deg.

polymerisation[43]. Condensation under molecular beam conditions yields a mixture which is closest to the molecular state; even the freezing of mixtures subjected to preliminary mixing in the gas phase can involve considerable separation into layers. Table 7 quotes as an example the results obtained in a study of certain halogenation and hydrohalogenation reactions of unsaturated compounds. The apparatus and technique have already been described[41].

Comparison of Tables 6 and 7 shows that in thoroughly blended mixtures the reactions can take place entirely at much lower temperatures. Bromination of ethylene and propene occurs at temperatures close to the melting points of the olefins. In the chlorine–cyclohexene system the reaction occurs in the solid phase at 98°K. This is the temperature of the glass–crystal phase transition. When these substances are frozen into two separate layers, the chlorination occurs at 169°K, i.e. near the melting points of the initial components. It is interesting that, due to their high reactivity, propene and bromine cannot be condensed on a surface cooled with liquid nitrogen at deposition velocities of 10^{17} mol. s^{-1}. This can only be done by reducing the rate of deposition by a power of ten.

Examination of Tables 6 and 7 reveals certain interesting peculiarities of chemical reactions at low temperatures.

1. Many chemical reactions of various types can occur spontaneously (in the absence of special initiation) in the condensed phase even at temperatures as low as the boiling point of liquid nitrogen.

2. These reactions often have high explosive velocities, which means that it is usually necessary to work with amounts of the order of 10^{-3}–10^{-4} mole.

3. A characteristic feature of low-temperature reactions involving addition of halogens to olefins is that they are quantitative and specific. As a rule only one substance (addition product) is obtained in a yield close to 100%. This may be compared with reactions in gas and even in liquid phases at elevated temperatures[16] in which a large amount of substitution products is usually obtained.

4. Low-temperature reactions are highly selective. For example, it has been shown that chlorine adds readily to ethylene but not to acetylene. Nitrogen tetroxide adds readily to propene but not to ethylene. Hydrogen bromide adds to isobutene in the dark and to propene only under the action of ultraviolet light, etc.

5. At low temperatures each reaction usually has a definite characteristic (critical) temperature, as a rule associated with a phase transition (fusion, polymorphic

transformation, crystallisation). It is interesting that in the reaction of nitrogen tetroxide (N_2O_4) with olefins the reaction temperature depends on the conditions of heat exchange between the system and the surrounding medium[44]. Improvement of heat exchange displaces the onset of reaction towards higher temperatures and conversely, when heat exchange with the surrounding medium is poor, the reaction occurs at lower temperatures. This effect of heat exchange conditions on reaction rate is usually characteristic of reactions which proceed by a thermal explosion mechanism[16].

In an examination of the peculiarities of spontaneous low-temperature reactions it is necessary to consider the origin of reactions at low temperatures and their mechanism. The solution of these problems was facilitated by a comparative study of the addition reactions of halogens to olefins at low and normal temperatures. Let us consider as an example the bromination of cyclohexene in carbon tetrachloride solution[45]. Study of this reaction in the temperature range 263–313°K (Fig. 11) showed that it has a negative temperature coefficient and that the reaction rate follows the equation $W = k(Br_2)^2(C_6H_{10})$. These findings can be explained on the hypothesis that the reaction proceeds via a stage in which an intermediate molecular complex forms by the mechanism

$$(1)\ Br_2 + C_6H_{10} \underset{k_2}{\overset{k_1}{\rightleftarrows}} [Br_2 \cdot C_6H_{10}];\quad (2)\ [Br_2 \cdot C_6H_{10}] + Br_2 \rightarrow \text{reaction product}, \qquad (I)$$

$$(1')\ 2Br_2 + C_6H_{10} \underset{k_2}{\overset{k_1}{\rightleftarrows}} [C_6H_{10} \cdot 2Br_2];\quad (2')\ [C_6H_{10} \cdot 2Br_2] \overset{k_3}{\rightarrow} \text{reaction product}, \qquad (II)$$

where $[Br_2.C_6H_{10}]$ or $[C_6H_{10}.2Br_2]$ are unstable molecular compounds. Application of the steady-state method to both mechanisms results in the same expression for the rate of consumption of bromine:

$$(3)\ -\frac{d(Br_2)}{dt} = Kk_3(Br_2)^2(C_6H_{10}),$$

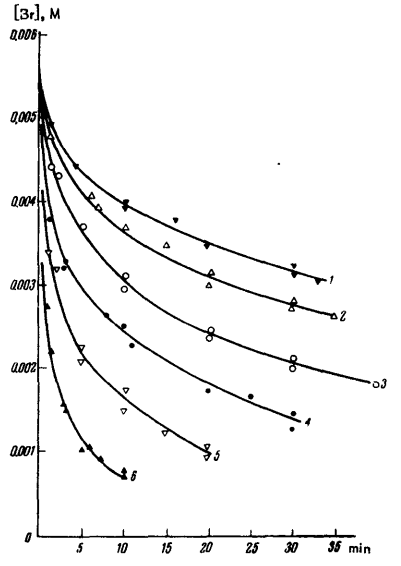


Fig. 11. Kinetic curves for the bromination of cyclohexane in carbon tetrachloride at different temperatures (°K):
1) 313; 2) 303; 3) 293; 4) 283; 5) 273; 6) 263.

where $K = k_1/k_2$ is the equilibrium constant for reactions (1) and (1'). This expression was obtained on the assumption that $K \ll 1$, and is consistent with the experimental order of reaction. Eqn. (3) shows that the experimental rate constant results from a combination of several constants:

$$k_{exp} = \frac{k_1k_3}{k_2} = \frac{k_1^0e^{-\frac{E_1}{RT}}k_3^0e^{-\frac{E_3}{RT}}}{k_2^0e^{-\frac{E_2}{RT}}} = k_0e^{-\frac{E_1-E_2}{RT}}e^{-\frac{E_3}{RT}} = k_0e^{\frac{\Delta H+E_3}{RT}},$$

where $\Delta H = E_1 - E_2$ is the heat of the complex-formation reaction. It may be assumed that over a small temperature range

$$\frac{\partial \ln k_{exp}}{\partial T} = \frac{\Delta H + E_3}{RT^2}.$$

The formation of molecular complexes occurs with evolution of heat ($\Delta H < 0$) and, when $E_3 < |\Delta H|$ and $E_3 + \Delta H < 0$, the rate of reaction falls with increase in temperature, i.e. there is a negative temperature coefficient.

The existence of a negative temperature coefficient is evidence that the reaction occurs in stages and shows that the heat of the rate-limiting stage, involving the formation of an intermediate, is higher than the activation energy for the conversion of the intermediate into the final reaction product. In a study of this reaction by differential thermal analysis (DTA) in a special vacuum reaction vessel it was shown that the reaction is nearly of first order. In the DTA method the observed temperature rise was mainly due to the heat of the rate-limiting stage. The result obtained is probably an indication that mechanism (II) is to be preferred for the bromination of cyclohexene.

The data on the kinetics of the bromination of cyclohexene in Fig. 11 show that the rate of reaction increases in accordance with the Arrhenius law as the temperature is reduced, but with, as it were, a negative activation energy $E = -12$ kcal mole^{-1}. This value is comparable to the heat of bromination of cyclohexene but exceeds the heat of formation of donor–acceptor complexes available in the literature, which are usually 1–5 kcal mole^{-1}.[13] This inconsistency suggests that in the halogenation reactions the intermediate molecular complex, whose structure is similar to that in the pre-reaction stage, is an aggregate (self-solvate) consisting of several bromine and cyclohexene molecules. As the temperature is reduced, the probability of the formation of such aggregates increases.

If the rate of halogenation of olefins is limited by the complex-formation stage, it follows in principle from the mechanism A + B $\rightleftharpoons$ (AB) $\rightarrow$ final product (A and B are the olefin and the halogen and AB is the intermediate complex) that conditions are possible in which the complex does not form and therefore the halogenation reaction cannot occur under the usual conditions. The bromination of tetrachloroethylene may be quoted as an example.

It has been demonstrated spectrophotometrically that at room temperature in the dark and in the absence of oxygen tetrachloroethylene does not react with bromine in carbon tetrachloride solution. When the mixture was kept at 253°K for 1.5 h, dibromotetrachloroethane was formed in 18% yield. This example clearly demonstrates the role of low temperature. In contrast to the usual postulates of classical chemical kinetics and our everyday experience, a reaction which does not take place in the liquid (condensed) phase begins to occur at a high rate when the temperature

is reduced. The occurrence of the bromination of tetrachloroethylene at low temperatures is evidence of the existence of highly active intermediate compounds responsible for the reaction and stable only at low temperatures. In the present author's view, such compounds are complexes of the donor–acceptor type.

On the other hand, it is also evident from the mechanism $A + B \rightleftharpoons (AB) \rightarrow$ final product that conditions may be found in which the relative rates of the individual reactions are such that the main effect is accumulation of the complex. When this is so, the use of low temperatures makes it possible to separate the complex-formation stage from the stage involving the conversion of the complex into final products. As an example, the results of a study of the bromine–propene system may be quoted[39].

Fig. 12 presents the results of the thermographic analysis of the bromine–propene mixture, with the components frozen into separate layers. The rapid reaction was preceded by two exothermic processes, one of which followed immediately after fusion of propene and occurred in the range between -185° and -156°C. It was shown that the evolution of heat in this temperature range is due to the dissolution of solid bromine in liquid propene and the formation of bromine–propene complexes, the heat of formation being about 5 kcal mole^{-1}. The second exothermic process occurred in the range between -156° and -125°C and preceded the reaction. This process may be associated with the segregation of the complexes into a separate phase and their association.

The use of low temperatures not only permits the separation of the stages involving the formation of the complex and the final product but also allows the accumulation of the intermediate complexes. For example, this can be done by repeated heating and cooling of the bromine–propene system in the temperature range between -196° and -156°C. The accumulation of complexes in this process is indicated by the fact that the amount of propene which may be evacuated from the bromine–propene system, for example at -145°C, decreases with the number of the above operations. The thermograms in Fig. 12 show that preliminary accumulation of complexes to a sufficiently high concentration results in the occurrence of rapid explosive reactions at -125°C. A relation between the complex-formation reaction and the bromination of propene is suggested by the fact that the magnitude of the exothermic peak at -125°C, corresponding to the reaction, depends on the number of heating and cooling cycles of the mixture in the temperature range between -196° and -156°C.

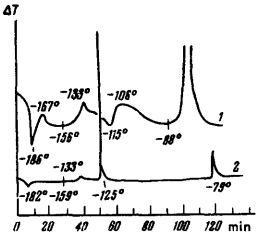


Fig. 12. Thermographic curves for bromine–propene mixtures:
1) specimens frozen in separate layers;
2) after preliminary mixing and accumulation of complex (temperatures in °C).

Additional proof of the participation of unstable molecular compounds in low-temperature halogenation of olefins was obtained with the aid of electronic absorption spectra, using bromination of propene as an example. In contrast to thermography, the spectroscopic method makes it possible to follow in greater detail the changes occurring in the initial molecules and in many cases helps elucidate the nature of the complexes formed[46].

The ultraviolet spectra of solid condensed films of bromine, propene, propane, and 1,2-dibromopropane were obtained with an SP-700 recording spectrophotometer. The test substances and their mixtures in various proportions were frozen in a vacuum cuvette on a quartz plate cooled with liquid nitrogen under conditions approximating to those in a molecular beam. The temperature of the film was measured with a thermocouple. At low temperatures propane is almost transparent up to 200 mμm. In the spectrum of solid propene there is a weak band in the region of 217–250 mμm. In the spectrum of solid bromine in amounts of 10^{-6} mole there is a band with an absorption maximum in the region of 280 mμm. When bromine is highly diluted with propane (1.8×10^{-7} mole of bromine and 4×10^{-4} mole of propane), the absorption in this region falls to an optical density of 0.01.

In the study of the bromine–propene system the initial components were frozen on to a cooled quartz plate in several successive layers. To ensure a more uniform distribution, bromine was diluted with propane in a number of experiments. The spectra of the bromine–propene system are presented in Fig. 13, which shows that in the spectrum of the mixture where the bromine was diluted with

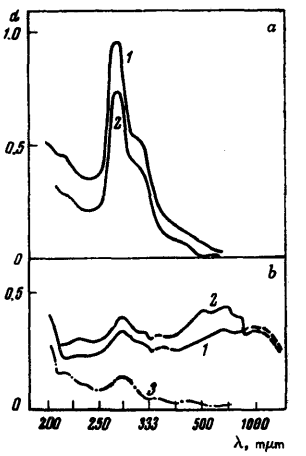


Fig. 13. Ultraviolet absorption spectra of the bromine (6×10^{-8} mole)–propene (9×10^{-4} mole) system:
a) spectra in the presence of added propane: 1) at 80°K; 2) mixture kept at 80°K for 1.5 h and then heated twice to 100°K [above m.p. of propene (83°K)], spectrum recorded at 73°K;
b) spectra of bromine–propene mixture (without propane): 1) at 80°K; 2) after 1.5 h at 80°K; 3) after heating to 100°K and recooling to 80°K, spectrum recorded at 80°K. The wavelength scale on the SP-700 spectrophotometer is expressed in cm^{-1}. In the Soviet chemical literature it is usual to express the wavelengths in the visible and ultraviolet spectra in millimicrons. The recalculation results in a non-linear scale.

propane there is an intense band in the region of 274 mμm. On the long-wavelength side of the band there is a distinct inflection in the region of 312.5 mμm. The absorption at the point of inflection is smaller at least by a factor of two than in the maximum of the band. When the temperature is raised, the band widens somewhat and its intensity falls irreversibly.

The spectrum of bromine–propene mixtures differs radically from that of the bromine–propane system. The much higher absorption intensity in the mixtures with propene indicates a pronounced donor–acceptor interaction between the bromine and propene. It may be supposed that in the bromine–propene system the bands in the region 274–312 mμm are due to 1 : 1 and 1 : 2 molecular charge-transfer complexes. The energy of an optical transition from the ground to an excited state in such donor–acceptor complexes is described by the approximate equation

$$h\nu = I - E - \frac{e^2}{r},$$

where I is the ionisation potential of the donor, E the electron affinity of the acceptor, and e^2/r the energy of the interaction of the components of the system, bearing opposite charges, at a distance r.[13,19] In binary complexes of bromine with various acceptors r varies in the range 3.6–4.5 Å, depending on the mutual disposition of the donor and acceptor molecules[22]. Adopting the average value of 4 Å for r and 1.2 eV for the electron affinity of bromine[22], the ionisation potential of propene was estimated as 9.3 eV from Eqn. (1) for the charge-transfer spectrum at $h\nu$ = 278 mμm. The satisfactory correlation of this value with $I_{C_3H_6}$ = 9.65 eV found for propene in the gas phase confirms the validity of the hypothesis that in the bromine–propene mixture molecular charge-transfer complexes are responsible for the absorption in the region 280–310 mμm. In the condensed phase the ionisation potential of the molecule should be lower than in the gas phase. This may be due to a certain energy gain resulting from the polarisation of the surrounding molecules by the positively charged ion and the free electron.

In the bromine–propene system undiluted by propane there are a number of new bands in addition to those at 278–312 mμm. The greatest interest attaches to a broad band in the region of 500–1000 mμm (Fig. 13, curve *1*). The intensity of this band is higher than that in the region of 278 mμm.

It is interesting that, on keeping the mixture at temperatures close to 77°K for a specified time, the intensity of the band in the region of 500–1000 mμm increases. On the other hand, if the mixture temperature is raised to 100°K (m.p. of propene is 88°K), the absorption in the range 500–1000 mμm vanishes irreversibly (Fig. 13*a*, curve *3*). The band in the region of 278 mμm persists to some extent. These results show that intermediate compounds which absorb between 500 and 1000 mμm are mainly responsible for the low-temperature bromination of propene.

The presence of the broad band between 500 and 1000 mμm in the spectrum of the bromine–propene mixture at low temperatures is evidence, in the author's view, that not binary complexes but strongly linked reactive aggregates of the type DADADADA, where D is the donor and A the acceptor, are responsible for the absorption. The existence of similar stable compounds with a chain structure at low temperatures has been described in the literature[47]. On energy grounds, at low temperatures such aggregates are more likely than binary compounds.

In associated compounds absorbing between 500 and 1000 mμm the molecular and intermolecular distances are markedly altered, with loosening of the double bond and its pronounced polarisation. Preliminary data from infrared spectra apparently confirm this conclusion because bands at lower frequencies have been detected in the spectra of frozen solid mixtures of bromine and propene in the region of double bond stretching vibrations (1632 cm^{-1}).

The formation of highly polarised associated molecular compounds of the donor–acceptor type in bromine–propene mixtures at low temperatures can probably facilitate electron transfer and the spontaneous appearance of ionised states. It is seen from the data in Fig. 13*b* that the energy of the non-equilibrium absorption of a light quantum (electron-transfer spectrum) at the long-wavelength edge of the absorption band of the aggregates at 2 μm is already as much as 0.5 eV. The energy of thermal excitation may be smaller than this and therefore it is reasonable to suppose that at low temperatures in strongly interacting complexes, formed during condensation with considerable evolution of heat, ions or radical-ions, facilitating the subsequent reaction, may form spontaneously.

The formation of molecular complexes with charge transfer probably plays a definite role also in liquid-phase halogenation of olefins at room temperature. This is indicated by the negative temperature coefficient characteristic of these reactions and the correlation between the rates of halogenation of olefins and their ionisation potentials I observed by the present author. As a rule, the lower the ionisation potential of the olefin, the higher is the rate of halogenation. For example the rates of bromination of various olefins increase in the series

ethylene	< propene	< but-1-ene	< isobutene	< trimethylethylene	< tetramethylethylene.
10.51	9.65	9.61	9.35	8.80	8.30 eV

A similar variation occurs also for olefin chlorination reactions. It was to be expected because a decrease of ionisation potential is accompanied by an increase in the concentration of complexes, in the degree of electron transfer, in dipole moment, etc. and ultimately the appearance of ionised states is facilitated. Definite correlations between olefin ionisation potentials, their polarity, and reaction temperatures obtain also in the low-temperature nitration of unsaturated compounds with nitrogen tetroxide.

It may be assumed that under the same conditions of heat exchange with the surrounding medium the reactivity of the olefin is higher the lower is the temperature of the onset of explosive reaction. The data in Table 6 suggest the following reactivity series for olefins in low-temperature nitration with nitrogen tetroxide

	isobutene <	but-1-ene <	propene,	hex-1-ene
Ionisation potential	9.35	9.61	9.65	9.59
Dipole moment	0.49	0.37	0.35	0.34

The higher is the polarity of the olefin, the lower is the temperature at which it can be nitrated. However, examination of more extensive experimental data shows

that the reactivity of olefins in relation to halogens and nitrogen tetroxide is not entirely determined by the dipole moment,

In the investigation of spontaneous low-temperature reactions it is important to obtain direct experimental proof of the formation of active centres when simple valence-saturated molecules interact in the absence of light. The author was able to demonstrate by the ESR method the formation of radicals in the interaction between tetranitromethane and cyclohexene, tetramethylethylene, and certain other olefins. The experiments were made in the dark at room temperature. Fig. 14 presents as an example the ESR spectrum obtained for mixtures of tetranitromethane with C_6H_{10}. It was shown spectrophotometrically that tetranitromethane can form charge-transfer complexes with olefins. The fact that an ESR signal can be obtained from such mixtures in the absence of light is an indication that, even in the absence of light, there is a complete electron transfer in the system, resulting in the formation of paramagnetic radical states. The ESR spectrum in Fig. 14 has a hyperfine structure consisting of five lines which probably indicates the interaction of the unpaired electron with the nuclei of two nitrogen atoms.

In conclusion it must be emphasised that the sum total of the experimental data, obtained mainly for halogenation and nitration of olefins, permits an examination of the mechanism of fast spontaneous low-temperature chemical reactions in the most general form. The first stage of the addition reaction occurs during the condensation of the starting materials and results mainly in the formation of molecular 1 : 1 or 1 : 2 compounds. In the halogenation of olefins the formation of such complexes constitutes only the initial stage of the reaction and cannot as a rule lead to the spontaneous occurrence of the reaction at low temperatures. The results of the spectroscopic study of the bromine–propene system show that at low temperatures not only molecular 1 : 1 or 1 : 2 compounds but also highly polar aggregates can form. The existence of such aggregates, which probably have a chain structure, is thermodynamically more favourable at low temperatures. Their formation should be accompanied by the evolution of considerable amounts of heat and may lead to the spontaneous appearance of active centres which initiate the addition reaction. The formation of final products usually occurs at higher temperatures at the instant of a phase transition. For this reaction to occur, it is probably necessary that a small activation barrier, associated with the elastic forces of the lattice, be overcome. The most favourable conditions for this occur in a phase transition, where molecules require a certain mobility. The presence of the previously formed chain structure at the instant of the phase transition retards molecular rotation and preserves their orientation which is favourable for the addition reaction. As a result, only one product is formed in quantitative yield. When the olefins and the halogen are frozen in separate layers, the stages involving the formation of the complexes and the final products may be separated. When the components are thoroughly mixed, for example on condensation under molecular beam conditions, all the stages merge and the halogenation reactions occur at temperatures close to that of liquid nitrogen. The occurrence of the reaction via a series of successive stages influences the activation energy for the overall process. The formation of unstable and probably strongly solvated exothermic molecular compounds decreases the effective activation energy by their heat of formation. When aggregates are formed, this effect is very considerable and may greatly facilitate low-temperature reactions.



Fig. 14. ESR spectrum of a mixture of tetranitromethane and cyclohexane at 293°K.

The results obtained suggest also a somewhat different mechanism for reactions in which there is donor–acceptor interaction at low temperatures. Apparently the role of molecular compounds and their aggregates does not consist solely in the facilitation of the initiation of the active centres, and their formation in all probability results in the conversion of the two-component system into a system of oriented molecules in which extensive electron transfer takes place and all the conditions required for reactions which proceed by the collective interaction mechanism, proposed earlier by Semenov to explain rapid low-temperature polymerisation reactions without activation energy[48], are thereby provided. In a polarised aggregate conditions are set up during the electron transfer process, as a result of the presence of markedly loosened and readily broken bonds, in which there is simultaneous dissociation of the double bonds and the bonds in the halogen molecules, new carbon–halogen bonds being formed. If the redistribution of electron density between the halogen and olefin molecules is insufficient for spontaneous propagation of the reaction by the above mechanism, then conversion of the chain, formed as a result of the intermolecular interaction, into the final product is possible by way of energy chains. The reactions examined are exothermic and are accompanied by the evolution of a considerable amount of heat. The energy evolved in the formation of the aggregate of the initial molecules can readily migrate at low temperatures along the chain of strongly interacting and favourably oriented molecules. As a result, neighbouring molecular complexes may be excited, and the entire chain may be converted into the final product virtually without activation energy.

Thus study of chemical reactions at low temperatures permits a closer approach to the solution of the principal problem in chemistry — the elucidation of the fundamental mechanism of the interaction of two species, and opens a route to fundamentally new chemical syntheses.

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