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Reactions of Epoxy-compounds by a Radical Mechanism

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Data on various methods for the initiation of radical reactions of epoxy-compounds, including their homopolymerisation, are reviewed systematically.
The bibliography comprises 134 references.

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I. INTRODUCTION

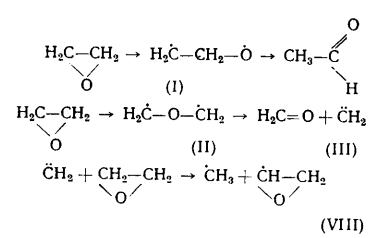
Much work has been done on the chemistry of epoxy-compounds. The reactions of these very simple heterocyclic compounds are treated from the standpoint of ionic mechanisms. With rare exceptions [5,13,14], no attention is devoted to radical reactions of epoxy-compounds in any of the monographs, reviews, and textbooks dealing with their chemistry [1-13]. Many investigators believe that such reactions are altogether impossible [15-18]. Similar views have been expressed by Staudinger and coworkers [15-17], who reported in the 1930's that radical type initiators, ultraviolet light, and sunlight do not influence epoxy-compounds and their reactions, in particular polymerisation, "occur only under the influence of appropriate catalysts". This situation did not alter in the course of the succeeding decade. Sorensen and Campbell [18] assert that only ionic catalysts are effective initiators of the polymerisation of epoxy-compounds. From time to time this view has been supported by new reports. Hopff and Zaner [second author not traced—name transcribed from Russian (Ed. of Translation)] [19] and also Oku et al. [20] did not observe the formation of acetophenone or a polymeric product from epoxyethylbenzene when azodi(isobutyronitrile) or benzoyl and lauroyl peroxides were used as initiators. The attempts to polymerise isoprene oxide [1,3-epoxy-2-methylbutane] by a radical mechanism in the presence of peroxides and azo-compounds were unsuccessful [21]. Epoxyethane does not react either with hydrogen peroxide (30%) or with lead dioxide, or with benzoyl peroxide [22]. In a recently published monograph dealing with the polymerisation of cyclic oxygen compounds [23] and also in the review by Frunze and Kurashev [14] the lack of reports on the homopolymerisation of epoxyalkanes initiated by radicals is pointed out.

Nevertheless, as early as 1918, Bodforss [24,25] obtained data which, in the light of modern concepts, may be explained as reactions of epoxy-compounds by a radical mechanism. The number of studies in which the reactions of epoxy-compounds are considered from the standpoint of radical processes has greatly increased in recent years. The investigation of chemical reactions of epoxy-compounds with participation of radicals is not only of theoretical but also of practical interest, since they have found application in many branches of the national economy.

The present review is a first attempt at a systematic account of reactions of epoxyalkanes involving a radical mechanism. Together with the description of the thermal, chemical, and photochemical initiation of the reactions, data are presented on the radiolysis of epoxy-compounds—a new branch of the radiation chemistry of heterocycles.

II. FORMATION OF RADICALS IN THE PYROLYSIS OF EPOXY-COMPOUNDS

Rice and Johnston [26] were some of the first investigators who noted the formation of radicals in the thermal decomposition of epoxy-compounds. Rice and Rice [27] detected free radicals in the pyrolysis of epoxyethane with the aid of a "metallic mirror". The rate of disappearance of the "metallic mirror" was higher than in the decomposition of other organic compounds, in particular acetaldehyde—a structural isomer of epoxyethane. Hence the authors concluded that a large number of radicals are formed in the decomposition of epoxyethane and proposed a mechanism of consecutive and parallel reactions [reactions (1)-(3)] in the pyrolysis of epoxyethane with participation of radicals of five types† (Table 1): ethylenoxy-radical [biradical (I)], hydroxydimethylene (II), carbene [methylene (III)], and methyl and epoxy-radicals (VIII).



(1)

(2)

(3)

There does not exist a unanimous view concerning the structure and reactions of pyrolytic free radicals. Rice

† There does not exist a single accepted terminology for the radicals arising in the cleavage of the epoxy-ring. In the present study an attempt is made to give a systematic account of such radicals and to name them on the basis of the nomenclature of organic compounds adopted by IUPAC [28,29]. In some cases the names of radicals adopted by individual authors were chosen and a number of trivial names have been proposed. Some of the radical names adopted in the original literature and not included in the Table have been retained in the text.

and Stalibaumer[30], Schumacher[31], Steacie[32], and Zimakov[13,33] give preference to radical (II). According to Zimakov[37], the biradicals (II), which are formed in the singlet state, influence the process only slightly since their lifetime is very short (about 10^{-13} s) and the metastable biradicals with a lifetime of 10^{-8} s make the main contribution to the pyrolytic reaction. To justify his view, Zimakov invoked Terenin's theory[38] of metastable biradicals produced as a result of the reversal of the spin of one of the two electrons and a transition of the biradical from the singlet to the triplet state, which in the case of epoxyethane can be represented as follows:

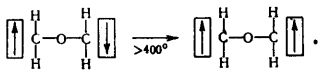
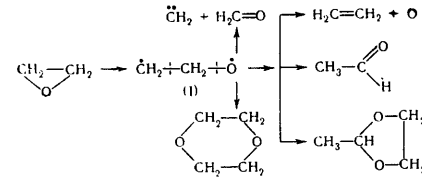


Table 1. Radicals formed from epoxy-compounds

№	Formula	Radical	References
(I)	$\dot{C}R_1R_2-CR_3R_4-\dot{O}$	Alkyl(aryl)ethyleneoxy	—
	$\dot{C}H_2-CH_2-\dot{O}$	Ethyleneoxy (biradical)	29
(II)	$\dot{C}R_1R_2-O-\dot{C}R_3R_4$	Oxydi[alkyl(aryl)]methylene	—
	$\dot{C}H_2-O-\dot{C}H_2$	Oxydimethylene	29
(III)	$\ddot{C}R_1R_2$	Carbene	28,34
	$\ddot{C}H_2$	Methylene	28
(IV)	$\dot{C}(=O)-H$	Formyl	29
(V)	$O=\dot{C}-CH_3$	Acetyl	29
(VI)	$R-\dot{C}H-C(=O)-H$	Alkylformylmethyl	29
(VII)	$R-C(=O)-\dot{C}H_2$	Keto-radical	20,35
		Acetonyl, R = CH_3	29
		Phenacyl, R = C_6H_5	29
(VIII)	$\dot{C}H-CH_2$ (O)	Epoxy	36
		1,2-Epoxyethyl	29
(IX)	$\dot{C}H-CH-CH_3$ (O)	1,2-Epoxy-1-propyl	—
(X)	$CH-\dot{C}-CH_3$ (O)	1,2-Epoxy-2-propyl	—
(XI)	$CH_2-CH-\dot{C}H_2$ (O)	Glycidyl (2,3-epoxypropyl)	—
(XII)	$CH_2-CH-CH_2-\dot{O}$ (O)	Oxyglycidyl (2,3-Epoxypropyloxy)	—
	OH	(2,3-Epoxypropoxyl)	—
(XIII)	$CH_3-\dot{C}H-\dot{C}H_2$	2-Hydroxypropyl	29
(XIV)	$\dot{C}H_2-CH_2-OH$	2-Hydroxyethyl	29
(XV)	$H-C(=O)-\dot{C}H_2$	Formylmethyl	29

Zimakov frequently emphasised[33,37,39] that "the formation of the stable dimethylene oxide biradical (II) in the pyrolysis of epoxyethane should in fact account for *all the characteristic features* (my italics—A. M.) of the pyrolytic reactions" of epoxyethane and various substances in its presence.

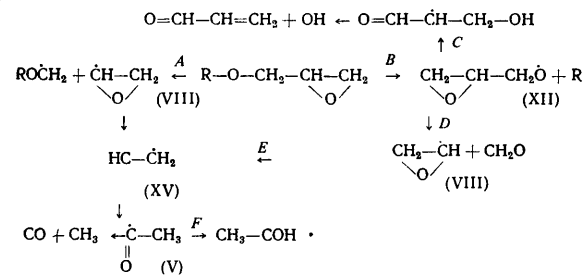
Malinovskii and Baranov demonstrated the inadequacy of the evidence for the decisive role of the biradical (II) in the pyrolysis of epoxyethane and epoxypropane in the presence of catalysts[40,41]. By adducing a number of pieces of evidence based mainly on the study of the composition of liquid-phase and gaseous decomposition products, Malinovskii and Baranov proposed other radical mechanisms for the pyrolysis of the above epoxy-compounds without the participation of oxydimethylene. Their mechanisms are based on the ethyleneoxy-biradical (I):



(4)

The authors note that the ethyleneoxy-biradical (I) is formed as an intermediate in the thermal decomposition of epoxyethane since "*only in this way* (my italics—A. M.) is it possible to explain" the presence of free oxygen and a large amount of ethylene and the formation of acetaldehyde and a cyclic acetal. The interpretation of the pyrolysis of epoxyethane and epoxypropane on the basis of the participation of ethyleneoxy-biradicals (I) provides a more convincing explanation of the formation of the final products, since the hypothesis of the oxydimethylene biradical (II) cannot account for the formation of all the reaction products.

In a series of studies by Neiman, Kovarskaya, Akutin, and coworkers[36,42-46] the thermal degradation of unhardened and hardened epoxy-resins was investigated. The composition of the gaseous pyrolysis products from the resins was the same for both hardened and unhardened resins regardless of the type of hardening agent employed (polyethylenepolyamine and maleic anhydride). According to the authors[36,42-46], the decomposition of the resin at 200–500°C is a free-radical process, which begins with the scission of the terminal part of the molecule and the formation of the epoxy-radical (VIII) (pathway *A*) and the oxyglycidyl radical (XII) (pathway *B*) according to the mechanism:



(5)

The radical (XII) can react in two ways: it can either isomerise via pathway *C* with formation of acrolein or it can decompose via pathway *D* into formaldehyde and the epoxy-radical (VIII). The latter isomerises via the formyl radical (XV) (pathway *E*) to the acetyl radical (V), which can in turn combine with hydrogen and form acetaldehyde or break down into carbon monoxide and a methyl radical. The suggested mechanism[36,42-46] does not postulate the cleavage of the three-membered ring at the C–C bond. The views of Neiman and coworkers on the isomerisation processes in the pyrolysis of epoxy-resins are shared by Anderson[47].

According to the literature, the mechanism of the thermal degradation or even the simplest epoxy-compound (epoxyethane) still remains controversial. This is indicated by (a) the difference between the radical and molecular pyrolysis products (furthermore, the complete set of products is not quoted in the reports of various workers), (b) the different interpretation of the formation of the same products, for example, carbon monoxide, methane, acetaldehyde, ethylene, acrolein, etc., and (c) the divergent views of investigators concerning the role of the methyl

radical: some believe that it interacts with the epoxyethane molecule, while others reject this hypothesis, etc. The considerable qualitative and quantitative differences between the reaction products from which inferences concerning the processes occurring were in fact mainly drawn led to the situation where almost every investigator proposes his own mechanism for the pyrolysis of epoxyethane. Malinovskii [5] rightly remarked that this state of affairs arose because of failure to take into account completely the reaction products and frequently because the experiments were performed under non-comparable conditions (purity of the products, design of the reactor, static or dynamic process conditions, different temperatures and pressures, presence and type of catalyst, etc.).

Furthermore, because of serious practical difficulties, epoxy- and other radicals have not been identified and it is so far impossible to distinguish between the conceivable involvement of radicals (I) and (II) in the pyrolysis of epoxyethane, for example. One cannot exclude the possibility that they coexist in different proportions, which are determined either by the electronic and molecular structure of the epoxy-compound or by the experimental conditions.

Speaking of epoxy-radicals, attention must be drawn to the following factors. The considerations concerning the formation of the oxydimethylene biradical described earlier [33,37,39] are based on the fact that in the epoxyethane molecule the C–C bond is least stable and therefore, on raising the temperature, is the first to break:

C–H 87.3 kcal mole^{-1}
C–O 70.0 kcal mole^{-1}
C–C 58.6 kcal mole^{-1}.

Table 2. Dissociation energies of the C–O bond in oxygen-containing heterocycles

Compound	Biradical formed	Bond dissociation energy, kcal mole^{-1}	No. of atoms in ring
Tetrahydropyran	$\dot{C}H_2(CH_2)_4\dot{O}$	71.2	6
Tetrahydrofuran	$\dot{C}H_2(CH_2)_3\dot{O}$	68.6	5
Trimethylene oxide	$\dot{C}H_2(CH_2)_2\dot{O}$	—	4
Epoxypropane	$\dot{C}H_2CHCH_3$ / $\dot{O}$	51.5	3
	$\dot{O}CH_2\dot{C}HCH_3$	50.5	
Epoxyethane	$\dot{C}H_2CH_2\dot{O}$	47.7	3

It is stated that the above estimates of bond strengths are consistent with the data of Gel'man [48] and Pauling [49]. However, more reliable studies [50] on the strength of the C–O bond in which account was taken of the ring size in cyclic ethers and epoxy-compounds yielded significantly different results. Table 2 shows that the maximum strength of the C–O bond is observed in six-membered cyclic ethers, where it reaches 71.2 kcal mole^{-1}. This value was in fact adopted [33,37,39] for the three-membered epoxy-ring. Actually, experiment shows [50] that, as the size of the ring of the heterocyclic oxygen-containing compound diminishes, the dissociation energy of the C–O bond falls sharply and for epoxy-compounds becomes approximately 50 kcal mole^{-1}. Thus the weakest bond in the epoxy-ring is C–O and not C–C as was believed [33,37,39]. In the vast majority of published reports and reports considered in the present review the preferential cleavage of the C–O bond in the epoxy-ring is noted, which agrees with the data of Gray and Williams [50].

III. RADICAL REACTIONS OF EPOXY-COMPOUNDS INITIATED BY PEROXIDES

Probably the first communication where it was noted that the epoxy-ring may be opened with formation of a polymer by a radical mechanism in the presence of initiators was that of Conant and Peterson [51] published in 1932. Even under severe conditions (12 000 atm., 168 h, 2% of benzoyl peroxide), epoxycyclohexane polymerised with difficulty, yielding a viscous liquid. After degassing in a vacuum at 100°C, a solid polymer soluble in benzene, chloroform, and ethyl and allyl ethers and insoluble in ethyl alcohol, acetone, and acetic anhydride was obtained.

The work of Conant and Peterson remained unnoticed and it was not until 30 years later that the radical reaction between epoxypropane and oct-1-ene initiated by t-butyl peroxide at 150°C was described [52]. According to gas–liquid chromatographic data, the reaction product is a ~ 4 : 1 mixture of 2-undecanone and 5-hydroxy-2-hexanone. The t-butoxy-radical formed in the decomposition of the peroxide abstracts a hydrogen atom from the second carbon atom [of epoxypropane (Ed. of Translation)] with formation of a 1,2-epoxy-2-propyl radical (X):

$$(CH_3)_3C\dot{O} + CH_3{-}CH(O){-}CH_2 \rightarrow (CH_3)_3COH + \underset{(X)}{CH_3{-}\dot{C}(O){-}CH_2}, \qquad (6)$$

which then isomerises to the keto-radical (VII):

$$CH_3{-}\dot{C}(O){-}CH_2 \rightarrow \underset{(VII)}{CH_3{-}C(=O){-}\dot{C}H_2}\cdot \qquad (7)$$

The radical (VII) attacks both the double bond of the olefin and the ring of the epoxy-compound, initiating the parallel competing reactions (8) and (9). 2-Undecanone is formed by reaction (8) from the keto-radical and oct-1-ene and 5-hydroxy-2-hexanone is formed by reaction (9) from the keto-radical and epoxypropane:

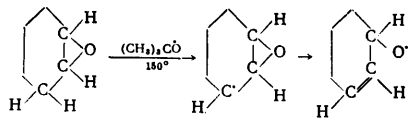
$$\rightarrow \begin{cases} CH_3{-}C(=O){-}\dot{C}H_2 \rightarrow \\ \quad CH_2{=}CH{-}C_6H_{13} \rightarrow CH_3{-}C(=O){-}CH_2CH_2{-}\dot{C}H{-}C_6H_{13} \xrightarrow{RH} CH_3{-}C(=O){-}CH_2CH_2{-}CH_2{-}C_6H_{13}, \qquad (8) \\ \quad CH_2{-}CH{-}CH_3 \rightarrow CH_3{-}C(=O){-}CH_2CH_2{-}CH(O\cdot){-}CH_3 \xrightarrow{RH} CH_3{-}C(=O){-}CH_2CH_2{-}CH(OH){-}CH_3\cdot \qquad (9) \end{cases}$$

To test their hypothesis concerning the pathway followed in the formation of the hydroxy-ketone, Gritter and Wallace investigated the reactions of epoxypropane with t-butyl peroxide in the presence of compounds with active hydrogen atoms and butyl groups. Large fragments—the residues of radicals (VII) and (XIII)—appeared in the final reaction products. The addition of 1,2-epoxybutane, 1,2-epoxyoctane, and epoxyethylbenzene to oct-1-ene by reaction (8) has also been achieved [53]‡. Aldehydes are absent from the reaction products, ketones alone being detected. This suggests a preferential removal of the hydrogen atom from the methine group in the epoxy-radical and its subsequent isomerisation to radical (VII).

Free radicals may abstract hydrogen from epoxy-compounds not only at the α- but also at the β-carbon atoms in relation to the oxygen atom, i.e. atoms in the allyl position with respect to the three-membered ring. This type of radical attack was observed by Sabatino and Gritter [54] in the reaction of t-butyl peroxide with epoxycyclohexane. It was suggested that, in consequence of the decyclisation and

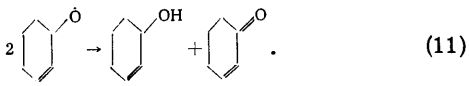
‡ The radical copolymerisation of epoxy-compounds is considered in the review of Frunze and Kurashev [14].

electronic isomerisation of the epoxy-ring, the initially formed radical isomerises to an unsaturated radical:



(10)

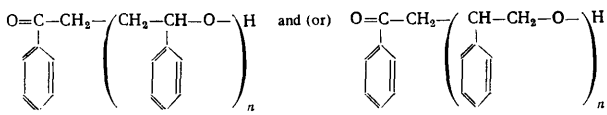
The authors explain the removal of a hydrogen atom from the β-carbon atom in the epoxycyclohexane molecule by postulating that the epoxy-ring behaves as a pseudo-olefin and the allyl position in olefins is known to be reactive with respect to radical attack [55,56]. Since cyclohex-2-en-1-one and cyclohex-2-en-1-ol are formed in small but approximately equal amounts, it may be supposed that the principal reaction undergone by the cyclohex-1-en-1-oxy-radical is disproportionation:



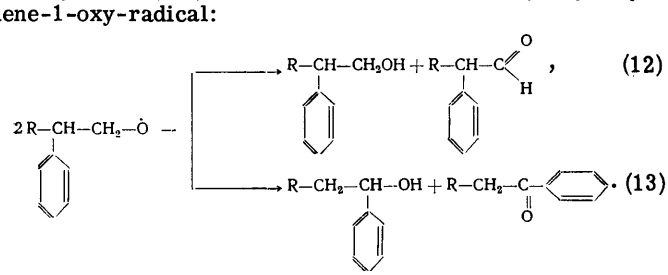
(11)

The main product of the reaction of t-butyl peroxide with epoxycyclohexane is cyclohexanone.

Using t-butyl and benzoyl peroxides as radical initiators, Oku et al. [20] achieved, in contradiction of the data of Hopff and Zaner [19], the polymerisation of epoxyethylbenzene and glycidyl phenyl ether. The only low-molecular-weight product isolated in the polymerisation of epoxyethylbenzene was acetophenone, which indicated the formation of the keto-radical (VII) as an intermediate. Polyepoxyethylbenzene had a molecular weight of 1500–2000. The infrared spectra of the polymer showed absorption bands at 3500 cm^{-1} (hydroxyl), 1720 and 1680 cm^{-1} (carbonyl), and 1030–1100 cm^{-1} (ether bond). These data suggest that the structure of the products formed by reaction (9) may be assigned to the polymer:



However, it has been established that there are about two hydroxy- and 1.5 carbonyl groups per polymer molecule. Probably these differences can be accounted for not only by the branching of the polyepoxyethylbenzene molecules but also by the disproportionation reactions of the phenylethylene-1-oxy-radical:

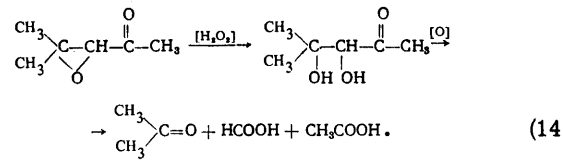


(12)

(13)

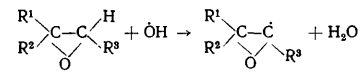
A similar mechanism of radical polymerisation in the presence of t-butyl peroxide has been suggested for glycidyl phenyl ether.

Razuvaev, Etlis, and coworkers investigated the interaction of hydroxy-radicals with a number of epoxyalkanes [57-60]. Since the carbonyl group lowers the reactivity of the oxygen atom of the epoxy-ring, t-butyl peroxide reacts with 3,4-epoxy-4-methylpentan-2-one with difficulty. However, the reaction of 3,4-epoxy-4-methylpentan-2-one with hydrogen peroxide takes place readily. A different reaction mechanism is proposed in this case: initially the epoxy-ring opens with formation of a keto-glycol, which is then oxidised to acetone and formic and acetic acids:



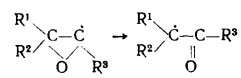
(14)

However, in most cases [57-59] the reactions of epoxy-compounds with hydrogen peroxide take place only on irradiation with ultraviolet light, which decomposes the peroxide into hydroxy-radicals. The hydroxy-radical formed abstracts a hydrogen atom with formation of a trialkylaryl-substituted epoxy-radical:



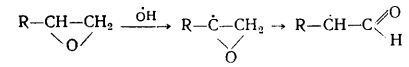
(15)

The latter may isomerise to a keto-radical. When an epoxyethane in which all the substituents were different was used, it was established [57] that the isomerisation is not accompanied by the migration of the R^1 or R^2 group to another carbon atom in the ring but takes place as a result of ring opening:



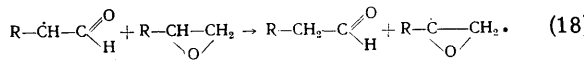
(16)

Unfortunately the authors do not consider the effect on the isomerisation process of the delocalisation of the unshared electron, which may alter to a considerable degree depending on the substituent. Thus the interaction of hydroxy-radicals with monosubstituted 1,2-epoxyalkanes also leads to the formation of epoxy-radicals but these isomerise to alkyl(aryl)formylmethyl radicals (VI) with migration of a hydrogen atom in the ring:



(17)

In contrast to trisubstituted epoxy-compounds, the products in this case are not ketones but aldehydes, which are probably formed by the reaction:

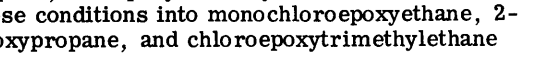


(18)

Furthermore, it is interesting to note that the products of the reactions of monosubstituted epoxy-compounds in which the substituents contain oxygen atoms (ether bond) include neither ketones nor aldehydes. Aldehydes may form in the isomerisation of epoxy-radicals but not the epoxy-compounds themselves, since the formation of propionaldehyde was not observed on irradiation of an aqueous solution of epoxypropane with ultraviolet light [59].

The oxidation of the aldehyde and (or) α-hydroxy-aldehyde formed as a result of the addition of a hydroxy-radical to radical (VI) probably leads to the formation of the corresponding acid, the reaction of which with the epoxyalkane yields an ester.

Photochemical liquid-phase chlorination of epoxyethane and epoxypropane with t-butyl hypochlorite was described by Walling and Fredricks [61] and that of epoxytrimethylethane and epichlorohydrin, by Razuvaev et al. [62] Epoxyethane, epoxypropane, and epoxytrimethylethane are converted under these conditions into monochloroepoxyethane, 2-chloroepoxypropane, and chloroepoxytrimethylethane

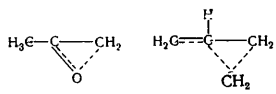


(19)

$$(CH_3)_3C\dot{O} + CH_2(O)CH{-}R \rightarrow CH_2(O)\dot{C}{-}R + (CH_3)_3COH, \quad (20)$$

$$(CH_3)_3COCl + CH_2(O)\dot{C}{-}R \rightarrow CH_2(O)CCl{-}R + (CH_3)_3C\dot{O}. \quad (21)$$

In the photochemical chlorination of the above epoxy-compounds with t-butyl hypochlorite there is preferential attack on the three-membered ring, the removal of a hydrogen atom from the ring, and the formation of α-chloroepoxy-compounds, while in the chlorination of methylcyclopropane the chlorine atom enters the methyl group. It is suggested [61] that the attack on the epoxy-ring is due to the high electron availability adjacent to the ether oxygen. Furthermore, the epoxy-radical (1,2-epoxy-2-propyl) formed in this process is evidently more stable than the isomeric glycidyl radical:



However, in the photochemical chlorination of epichlorohydrin with t-butyl hypochlorite, the former behaves like methylcyclopropane, since in this case the main product was 3,3-dichloroepoxypropane [62], i.e. the glycidyl radical (XI) and not the epoxy-radical was formed.

Furthermore, in contrast to the observations of Gritter and Wallace [52], the radical (X) formed by reaction (20) did not isomerise to the keto-radical but reacted with t-butyl hypochlorite or its decomposition products to form α-chloroepoxy-compounds. These compounds then readily isomerised to carbonyl compounds with migration of the chlorine atoms to an adjacent carbon atom: chloroepoxyethane was converted into chloroacetaldehyde, and chloroepoxytrimethylethane into chloroisopropyl methyl ketone [62]:

$$(CH_3)_2C(O)CCl{-}CH_3 \rightarrow (CH_3)_2CCl{-}C(=O){-}CH_3. \quad (22)$$

These data confirm yet again the view that the mechanism of the isomerisation of epoxy-compounds is determined primarily by their electronic structure.

The experimental data examined above show that the free-radical reactions of epoxy-compounds in the presence of initiators may be divided into three types: (1) reactions with ring opening as a result of attack by a free radical; (2) reactions involving the abstraction of a hydrogen atom from the α-carbon atom of the ring; (3) reactions involving the abstraction of hydrogen atoms in the allyl position with respect to the oxygen atom of the epoxy-ring, i.e. in the β-position with respect to the ring. The products contain hydroxy- and carbonyl-groups. The formation of carbonyl compounds from epoxy-compounds is due to the isomerisation of epoxy-radicals.

IV. PHOTOCHEMICAL REACTIONS OF EPOXY-COMPOUNDS BY A RADICAL MECHANISM

The photochemical decomposition of epoxyethane in the gaseous state was investigated by Phibbs et al. [63] Since epoxyethane has only one absorption band at 1713 Å, [64,65] its decomposition was sensitised by mercury vapour. The principal reaction products proved to be hydrogen, carbon monoxide, acetaldehyde, and a polymer; smaller amounts of methane, formaldehyde, and C_2 hydrocarbons were also detected. Bearing in mind the composition of the photolysis products and only slight dependence of their yield on pressure, the authors [63] believe that the isomerisation and decomposition processes are based on the reactions of excited epoxyethane molecules,

$$Hg(^3P_1) + CH_2(O)CH_2 \rightarrow CH_2(O)\dot{C}H + H + Hg(^1S_0), \quad (23)$$

and the polymerisation process has a free-radical mechanism. Homer and Noyes [66] carried out direct photochemical decomposition of epoxyethane at a wavelength < 2000 Å in the gas phase (10–100 mmHg, 27–250°C) and in a mixture with dimethylmercury. The reaction products were hydrogen, carbon monoxide, methane, ethane and smaller amounts of formaldehyde, acetaldehyde, and more complex aldehydes. The primary decomposition products are probably methyl and formyl radicals:

$$CH_2(O)CH_2 \xrightarrow{h\nu} \dot{C}H_3 + H\dot{C}O. \quad (24)$$

(IV)

Since the heat of dissociation of the formyl radical (IV) is close to zero and therefore its thermodynamic stability is almost independent of temperature, it should decompose as follows:

$$H\dot{C}O \rightarrow CO + \dot{H}. \quad (25)$$

The methyl radical mainly abstracts a hydrogen atom forming methane and to a lesser extent dimerises to ethane. With increase of the intensity of illumination and temperature, the methane : ethane ratio increases. The contribution of the reaction

$$H + CH_2(O)CH_2 \rightarrow H_2 + \dot{C}H(O)CH_2 \quad (27)\S$$

(VIII)

also increases with temperature. Part of the epoxy-radicals (VIII) decompose with elimination of carbon monoxide:

$$CH_2(O)\dot{C}H \rightarrow \dot{C}H_3 + CO \quad (28)$$

while others are stabilised by combining with other radicals and atoms.

The photochemical decomposition of epoxyethane sensitised by mercury [67] involves the formation of hydrogen, methane, ethane, propane, ethylene, carbon monoxide, acetaldehyde, higher homologues of acetaldehyde, and small amounts of a ketone. Cvetanovic [67] believes that the principal primary step is the decomposition of the excited epoxyethane molecule by reactions (23)–(25). He also postulates the molecular breakdown of epoxyethane into hydrogen and keten to a slight extent.

Evidently the mechanism of the photolysis of epoxyethane is complex and inadequately investigated. In order to avoid the effect of secondary reactions, Roquitte [68] subjected epoxyethane, tetradeuteroepoxyethane, and their mixtures to pulse photolysis at an effective wavelength of 1900 Å and energies of the light pulse up to 2160 J with the lifetime of a single pulse 44 ms. Hydrogen, methane, ethane, ethylene, carbon monoxide, and carbon dioxide were found among the photolysis products, but there were no aldehydes. The author believes that three parallel competing processes take place under these conditions:

$$CH_2(O)CH_2 \xrightarrow{h\nu} \begin{cases} \rightarrow CH_3 + CO + H, & (29) \\ \rightleftarrows CH_2{=}CH_2 + O, & (30) \\ \rightarrow H_2 + C_2H_2O. & (31) \end{cases}$$

§ Eqn. (26) is missing in the original Russian text (Ed. of Translation).

The principal stage of the process is reaction (29), since a high yield of carbon monoxide and its increase with light intensity are observed. Furthermore, 70% of hydrogen is also formed by reaction (29) and 30% as a result of the primary molecular reaction (31). The authors believe that the effect of reaction (30) is slight because of its reversibility. The relative quantitative contributions of reactions, (29), (30), and (31) to the pulse photolysis of epoxyethane are estimated as $2.3:1:\ll 1$. Reaction (29) is analogous to the process described for photolysis with a low intensity of illumination[66] and reactions (30) and (31) were discussed by Cvetanovic[67,69]. In the photolysis of an equimolar mixture of C_2H_4O and C_2D_4O it was established[68] that 82% of the methane was formed from methyl radicals [reaction (29)] and 17.5% was formed with participation of methylene. The appearance of methylene can be explained by the decomposition of the excited keten molecule formed by reaction (31):

$$CH_2{=}C{=}O^* \rightarrow \dot{C}H_2 + CO. \qquad (32)$$

Carbonyl compounds, carbon monoxide, hydrogen, ethylene, and alkanes were the products of the photochemical decomposition of *trans*-2,3-epoxybutane in the gas phase[70]. When oxygen was added (about 0.5 mmHg), methanol was the principal photolysis product. An increase of pressure in the irradiation of pure *trans*-2,3-epoxybutane sharply reduces the yields of carbon monoxide, ethylene, propane, and particularly carbonyl compounds. It is believed that, with increase of pressure, the fragment C_3H_5O loses its excess energy in collisions and is stabilised by conversion into radical (IX), while at a low pressure it can isomerise to radicals (VI) and (VII) or decompose by the reaction

$$CH_3{-}\underset{\diagdown O \diagup}{CH}{-}\dot{C}H \rightarrow C_2H_4 + \dot{C}HO \qquad (33)$$

and further by reaction (25) or it can form $CH_3{-}C(=O){-}H$ and $C_2H_5{-}C(=O){-}H$ by reacting with $\dot{C}H_3$ and $\dot{C}_2H_5$.[67]

With increase of pressure, the quantum yield of the main photolysis product (isobutyraldehyde), formed at a low pressure [by the reaction of radicals (VI) with $\dot{C}H_3$] diminishes, since under these conditions the concentration of radicals (VI) falls. Cvetanovic and Doyle postulated the dissociation of the C–O bond in the epoxy-ring in the photolysis of *trans*-2,3-epoxybutane and the formation of "triplet biradicals" (I), similar to those which arose in the reaction between oxygen atoms and but-2-ene isomers ($CH_3{-}\underset{\dot{O}}{CH}{-}\dot{C}H{-}CH_3$).[71] These radicals underwent intramolecular rearrangement and hardly decomposed. The dissociation of the C–H bond in the molecules of the epoxy-compound investigated was not observed during photolysis.

The gas-phase photolysis of glycidic aldehyde, one of the simplest of the bifunctional epoxy-compounds, was investigated by Goodspeed and Blacet[72] (irradiation at wavelengths of 3130 and 2654 Å, pressure 16–27 mmHg, 77–127°C). The decomposition of the aldehyde was represented by the following mechanism:

$$CH_2{-}\underset{\diagdown O \diagup}{CH}{-}CHO \xrightarrow{h\nu} \begin{cases} \rightarrow \underset{\diagdown O \diagup}{CH_2{-}\dot{C}H} + \dot{C}HO, & (34) \\ \rightarrow \left[\underset{\diagdown O \diagup}{CH_2{-}CH_2}{-}C{=}O\right]^* \xrightarrow{M} O{-}C{=}O \;(H_2C{-}CH_2), & (35) \\ \rightarrow C_2H_4 + CO_2, & (36) \\ \rightarrow CH_3CHO + CO. & (37) \end{cases}$$

(VIII)

The radical (VIII) decomposes by reaction (28) and methyl and formyl radicals react with glycidic aldehyde giving rise to methane, carbon monoxide, CH_3CO, and hydrogen and to carbon monoxide and $CH_3\dot{C}O$ respectively. It was established that at 3130 Å reactions (36), (37), and (34) consume 75%, 5%, and 10% of the energy absorbed respectively. Photochemical dissociation reactions (36) and (37) of the liquid propiolactone are also suggested.

In contrast to previous studies, where the epoxy-compounds were photolysed in the gaseous state, Sabatino and Gritter[54] initiated the free-radical reactions of a number of epoxy-compounds in the liquid phase at a wavelength of 2537 Å. The authors believe that pulse illumination and low conversions reduced the likelihood of secondary reactions. Epoxypropane was irradiated both in the presence and absence of oct-1-ene; epoxycyclohexane and epoxyethylbenzene were irradiated in a pure form. The reaction products suggested that the decomposition of all the epoxy-compounds was of the same type.

Like Cvetanovic[70], Gritter and Sabatino¶ believe that the most important factor is the primary homolytic cleavage of one or other C–O bond in the ring with formation of biradicals of type (I). To account for the radical mechanism of the photolysis of epoxypropane, for example, and the formation of a ketone, aldehydes, an alcohol, and a dimer, they suggest the following sequence of stages:

$$CH_3{-}\underset{\diagdown O \diagup}{CH}{-}CH_2 \begin{cases} \xrightarrow{h\nu} CH_3{-}\underset{\dot{O}}{CH}{-}\dot{C}H_2, & (38) \\ \xrightarrow{h\nu} CH_3{-}\dot{C}H{-}\underset{\dot{O}}{CH_2}, & (39) \end{cases}$$

$$CH_3{-}\underset{\dot{O}}{CH}{-}\dot{C}H_2 + CH_3{-}\underset{\diagdown O \diagup}{CH}{-}CH_2 \rightarrow CH_3{-}\underset{\dot{O}}{CH}{-}CH_3 + CH_3{-}\dot{C}(\diagdown O \diagup){-}CH_2, \qquad (40)$$

$$2CH_3{-}\underset{\dot{O}}{CH}{-}CH_3 \rightarrow CH_3{-}\underset{O}{C}{-}CH_3 + CH_3{-}\underset{OH}{CH}{-}CH_3, \qquad (41)$$

$$CH_3{-}\dot{C}H{-}\underset{\dot{O}}{CH_2} + CH_3{-}\underset{\diagdown O \diagup}{CH}{-}CH_2 \rightarrow CH_3{-}CH_2{-}\underset{\dot{O}}{CH_2} + CH_3{-}\dot{C}(\diagdown O \diagup){-}CH_2, \qquad (42)$$

$$CH_3{-}\dot{C}(\diagdown O \diagup){-}CH_2 \rightarrow CH_3{-}\underset{O}{C}{-}\dot{C}H_2, \qquad (7)$$

$$CH_3{-}\underset{O}{C}{-}\dot{C}H_2 + \dot{C}H_2{-}\underset{O}{C}{-}CH_3 \rightarrow CH_3{-}\underset{O}{C}{-}CH_2{-}CH_2{-}\underset{O}{C}{-}CH_3, \qquad (43)$$

$$CH_3{-}\underset{O}{C}{-}\dot{C}H_2 + CH_3{-}\underset{\diagdown O \diagup}{CH}{-}CH_2 \rightarrow CH_3{-}\underset{O}{C}{-}CH_3 + CH_3{-}\dot{C}(\diagdown O \diagup){-}CH_2. \qquad (44)$$

Referring to Walling[73], the authors state that the rearrangement of the initially formed biradicals into a ketone and an aldehyde, involving the migration of a hydrogen atom, is exceptionally fast. The acetonyl radical interacts with oct-1-ene by reaction (8). Although the authors attempted to exclude the occurrence of secondary reactions, Table 3 shows that in the photolysis of epoxypropane it was impossible to achieve this completely. The high content of acetone in the photolysis products (about 70% when acetonylacetone is allowed for) introduces additional difficulties into the interpretation of the mechanism of the photolysis, since acetone may be consumed in the photosynthesis of acetonylacetone[74,75]. Under the experimental conditions where the system was irradiated with light corresponding to the absorption band of ketones, acetone may also have served as a source of acetonyl radicals but this possibility was not taken into account; the effect of oxygen on various radicals and the process as a whole is obscure (the report does not state that the photolysis was carried out in a vacuum).

¶ J. Org. Chem., 29, 1965 (1964) (Ed. of Translation).

Although the suggested mechanism, as in very many other cases, is speculative and controversial and requires experimental confirmation, nevertheless the important role of acetonyl radicals in it and the preferential dissociation of C–O bonds are noteworthy. If 1-C–H and especially 2-C–H bonds were dissociated (which does not entail the isomerisation of the ring), it would be difficult to account for the formation of alcohols, while the dissociation of the C–C bond excludes the formation of even one of the observed reaction products.

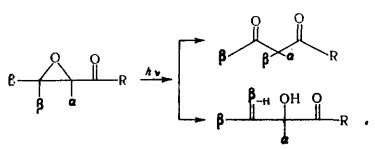
Table 3. Composition of the photolysis products of epoxypropane, epoxycyclohexane, and epoxyethylbenzene

Reactant	Reaction products	Site of dissociation	Conversion, %
Epoxypropane	acetone	C–1–O	0.28
	isopropyl alcohol	C–1–O	0.21
	acetonylacetone	C–1–O	0.22
	propionaldehyde	C–2–O	0.01
	propyl alcohol	C–2–O	0.01
Epoxycyclohexane	cyclohexanone	C–O	0.23
	cyclohexanol	C–O	0.14
Epoxyethylbenzene	acetophenone	C–1–O	0.03
	2-phenylethanol	C–1–O	0.14
	1-phenylethanol	C–2–O	0.13

Earlier it was noted that the absorption band of the epoxy-group in the electronic spectrum is in the far ultraviolet and the position of its absorption maximum does not differ markedly from that corresponding to the ethylene double bond. The conjugation of the ethylene double bond with the carbonyl group in the molecule of an $\alpha\beta$-unsaturated carbonyl compound results in a considerable shift of the absorption bands of both groups towards longer wavelengths[76]. A similar effect may be observed in $\alpha\beta$-epoxy-ketones where the ethylene double bond is replaced by an epoxy-group[72,77], which makes it possible to carry out the photolysis with ultraviolet light at longer wavelengths.

One of the first investigations of the photochemical reactions of $\alpha\beta$-epoxy-ketones was carried out by Bodforss[24,25].

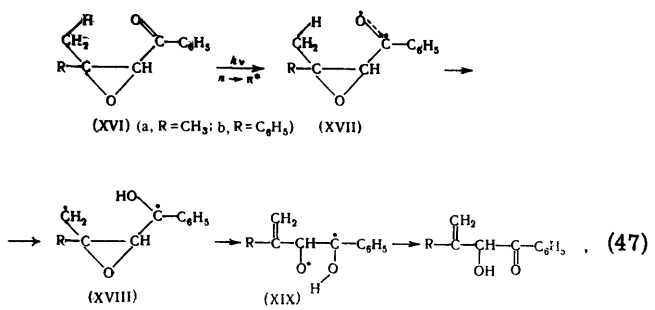
The photochemical rearrangement of $\alpha\beta$-epoxy-ketones may lead to the formation of a β-diketone [reaction (45)][24,78–81] or a keto-alcohol [reaction (46)][79]:



(45)

(46)

The formation of β-diketones entails the migration of the substituent from the β-carbon atom in relation to the carbonyl group to the α-carbon atom. The possibility of absorption of ultraviolet light by the epoxy-ring is disregarded and its cleavage is attributed to the effect of the carbonyl group[79,81]. The opening of the epoxy-ring in 1,2-epoxy-2-methylpropyl phenyl ketone (dimethylacrylophenone oxide) (XVIa) and 1,2-epoxy-2-phenylpropyl phenyl ketone (dypnone oxide) (XVIb) takes place as a result of the $n\rightarrow\pi^*$ excitation of the carbonyl group and subsequent rearrangement of the molecule by mechanism (47).[79] As a result of intramolecular photochemical dehydrogenation, in which the excited carbonyl group of compound (XVII) abstracts a hydrogen atom from the methyl group, the biradical (XVIII) is formed. The presence of an unpaired electron at the methylene group linked to the epoxy-ring favours the homolytic dissociation of the C–O bond, giving rise to the biradical (XIX) in which the semiquinone group $\dot{C}$–OH derived from the carbonyl group responsible for the photochemical dehydrogenation remains unchanged. In the last stage intramolecular disproportionation leads to the final reaction product:



(XVI) (a, R = CH_3; b, R = C_6H_5) (XVII) (XVIII) (XIX) (47)

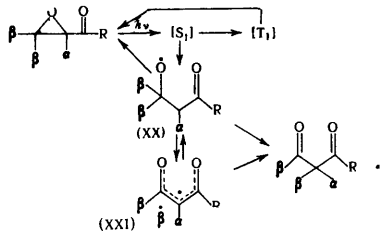
Together with the intermolecular photochemical dehydrogenation reactions known previously, reaction (47)[82] may be used for preparative intramolecular photochemical dehydrogenation of $\alpha\beta$-epoxy-ketones[79].

As a result of the photochemical reaction involving the excitation of the non-bonding electrons of the oxygen atom in the carbonyl group, 3,4-epoxy-4-phenyl-2-pentanone and 3,4-epoxy-4-methyl-2-pentanone rearrange to β-diketones [reaction (45)] with migration of the methyl group[78,79,83] in contrast to reaction (47). In a discussion of the reactivity of the carbonyl group in the excited $n\rightarrow\pi^*$ state it was noted[79,84,85] that the groups attached to the carbon atom adjoining the excited C=O group may undergo homolytic cleavage. Evidently reaction (45) does in fact begin with such cleavage. The cleavage of the C–O bond in the epoxy-ring, in contrast to the abstraction of a hydrogen atom from the γ-carbon atom in compound (XVI), is attributed[79] to an excited π^* electron which is more localised at the carbonyl group of 3,4-epoxy-4-methyl-2-pentanone and 3,4-epoxy-4-phenyl-2-pentanone and to the greater probability of C–O dissociation, since in compound (XVI) the excited electron is delocalised over both the carbonyl and phenyl groups and its effect is reduced.

In a study of the photochemical rearrangements of $\alpha\beta$-epoxy-ketones to β-diketones, an unusual sequence of various β-groups as regards their capacity for migration was observed[78,79,81,86,87]: diphenylmethyl and benzyl > hydrogen > methylene > methyl > phenyl.

An important aspect of the mechanism of the photochemical rearrangement of epoxy-ketones was established by Markos and Reusch[81] [reaction (48)][81], who observed that the photochemical reactions of $\alpha\beta$-epoxy-ketones take place via the singlet excitation of the molecule [S] and the intermediate state (XX), bypassing the triplet state [T], since

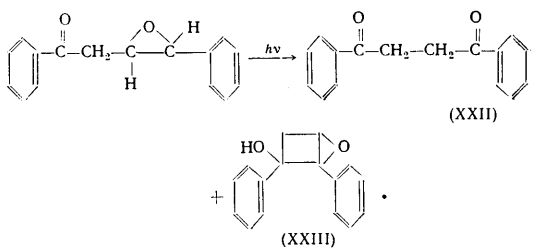
the rearrangement of epoxy-ketones proved to be insensitive to the presence of oxygen, a change of solvent, and the addition of reagents quenching triplet states.



(48)

To account for the anomalous capacity for migration and the formation of fragmentation products, it was assumed that the migrating group is a radical and that a radical pair is formed in the cage (XXI) from the intermediate state (XX). Unsaturated $\alpha\beta$-epoxy-ketones were much more stable in relation to the $n\rightarrow\pi^*$ excitation of the carbonyl groups than their saturated analogues[87].

The photochemical rearrangement of $\beta\gamma$-epoxy-ketones, for example *trans*-3,4-epoxy-1,4-diphenylbutan-1-one, leads to the formation of a γ-diketone (XXII) and an alcohol to which the structure (XXIII) is attributed:



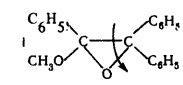
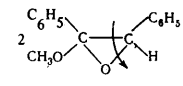
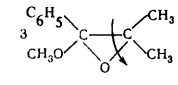
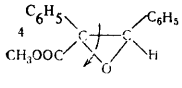
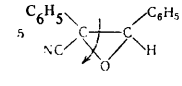
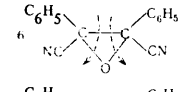
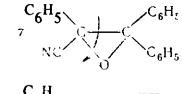
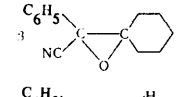
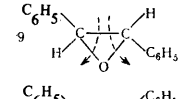
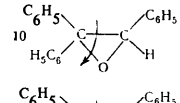
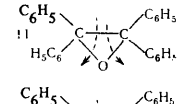
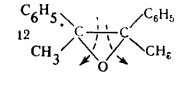
(49)

It is suggested[88] that epoxycyclobutane may be formed by reaction (47) with the sole difference that the semiquinone reacts with the unshared electron of the γ-carbon atom, forming a new C–C bond.

Temnikova and coworkers[89–93] and a group of American investigators[94–100] obtained new, novel data on the radical mechanism of the photolysis of epoxy-compounds. They made the interesting observation of the intermediate formation of carbenes on irradiation with ultraviolet light of a number of epoxyethane derivatives (Table 4). The arrows indicate the chemical bonds in the three-membered ring which are preferentially cleaved during photolysis, i.e. the arrow separates the carbene formed. The remaining molecular fragment rearranges very rapidly to the corresponding carbonyl compound. As a rule, all the epoxy-compounds were irradiated in methanol or olefin solution. The type of solvent was probably dictated by the endeavour to demonstrate the existence of carbenes on the basis of the composition of the product formed by typical secondary reactions. Indeed, irradiation of epoxy-compounds 1 and 11 (Table 4) in methanol gave an almost quantitative yield of methoxydiphenylmethane[89,94], while irradiation of a solution of epoxy-compound 5 gave α-methoxyphenylacetonitrile[99]. In the presence of olefins the photolytic decomposition of epoxy-compounds takes place with formation of the corresponding cyclopropane derivatives, which is generally regarded as proof of the presence of carbenes. Thus the photolysis of the cyanoepoxy-compound 6 (Table 4) in tri- and tetra-methylethylene gave good yields (80%) of cyclopropane derivatives with the cyano-group attached to the three-membered ring. This process has been suggested as a preparative method for the synthesis of phenylcyanomethylene[92].

Convincing direct evidence for the formation of carbenes in the photolysis of epoxy-compounds was obtained recently. The carbenes were identified by a luminescence technique and by an ESR method in irradiated epoxy-compounds 10 and 11 (Table 4) at −196°C in methylcyclohexane solution. The Figure shows the luminescence spectrum of the irradiated epoxy-compound 11 (Table 4). The

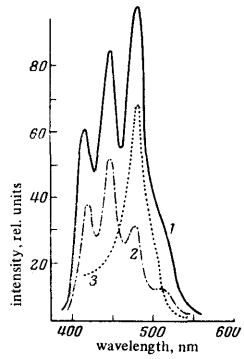
Table 4. Epoxy-compounds yielding carbenes on photolysis

Formula	Epoxy-compound	Solvent, concn.	decomp. pathway	References
1 	epoxy-1-methoxy-1,2,2-triphenylethane	methyl alcohol, trimethylethylene	*B*	89
2 	epoxy-1-methoxy-1,2-diphenylethane	trimethylethylene, tetramethylethylene	*B*	91
3 	epoxy-1-methoxy-2,2-dimethyl-1-phenylethane	trimethylethylene	*B*	89
4 	epoxy-1-methoxy-carbonyl-1,2-diphenylethane	methyl alcohol, trimethylethylene	*A*	93,99
5 	1-cyanoepoxy-1,2-diphenylethane	trimethylethylene, tetramethylethylene, methyl alcohol (0.1 M), 2,3-dimethylbut-2-ene (0.5 M)	*A*	91,94 98,99
6 	1,2-dicyanoepoxy-1,2-diphenylethane	trimethylethylene, tetramethylethylene	*A, B*	92
7 	1-cyanoepoxy-1,2,2-triphenylethane	methyl alcohol (0.3 M), 2,3-dimethylbut-2-ene (0.3 M), 2-methylbut-2-ene	*A*	94,98 99
8 	1-cyanoepoxy-2,2-pentamethylene-1-phenylethane	methyl alcohol (0.3 M), 2,3-dimethylbut-2-ene (0.3 M)	*A*	99
9 	*trans*-epoxy-1,2-diphenylethane *trans*-(stilbene oxide)	2-methylbut-2-ene	*A,B*	94
10 	epoxytriphenylethane	methylcyclohexane (10^{-4} M), 2-methylbut-2-ene + benzene, 2-methylbut-2-ene	*A*	94,100
11 	epoxytetraphenylethane	methyl alcohol + benzene and methylcyclohexane (10^{-4} M)	*A,B*	94,100
12 	epoxy-1,2-dimethyl-1,2-diphenylethane		*A,B*	96

authors[100] showed that part of the total luminescence spectrum corresponds to the phosphorescence of benzophenone (the carbonyl-containing fragment of the molecule of compound 11 after its photochemical decomposition) and another part to the fluorescence of the diphenylcarbene biradical (III). The latter spectrum corresponded fully to the luminescence spectrum of diphenylcarbene obtained by a different method[101,102]. According to the ESR spectra of the irradiated solution of compound 11, diphenylcarbene has a triplet ground state (the spins of the free electrons are parallel), i.e. it may be regarded as a biradical.

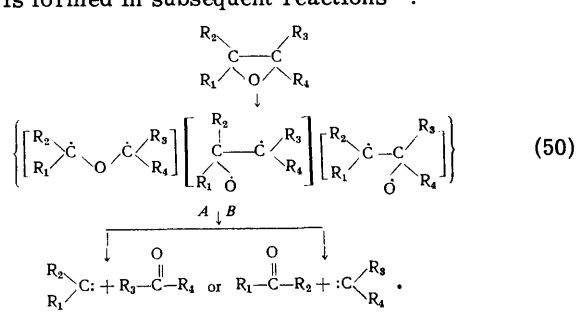
Thus, together with photolytic cleavage of diazo-compounds and ketones, a new source of biradicals with a wide variety of substituents has been found, namely epoxy-compounds. The photochemical method for the generation of carbenes from epoxy-compounds was discovered recently and is therefore not included in Kirmse's monograph[34].

The experimental data from the investigations considered[89-99] permit certain conclusions concerning the radical mechanism of the photolysis of epoxy-compounds. Although in all these investigations[89-99] without exception, starting with the first report by Kristinnsson and Griffin[94], the dissociation of the C–C bond is suggested as the primary step in the photolysis of the epoxy-rings, there is no convincing evidence for the reaction by this pathway. It appears desirable to represent the photolysis of epoxy-compounds by mechanism (50). We may also note that later Griffin and Kristinnsson changed their view on the primary stage of the process[100].



Luminescence spectra of the photolysis products of epoxytriphenylethane: *1*) overall luminescence spectrum; *2*) phosphorescence spectrum; *3*) fluorescence spectrum (the difference between the total luminescence and phosphorescence). Conditions of photolysis: 10^{-4} M solution of epoxytetraphenylethane in methylcyclohexane; temperature 77°K; duration of irradiation 20 s; wavelength 2537 Å.

The nature and number of substituents of the epoxy-ring are of decisive importance for the occurrence of reaction (50) by pathways *A* and *B* and for the very possibility of the formation of the carbene. Examination of data on the photochemical reactions of epoxy-compounds shows that carbenes are not formed from epoxyethane and its monosubstituted derivatives. On the other hand, methylene appearing in the photolysis of epoxyethane is not a product of the direct breakdown on the epoxy-compound [reaction (32)] but is formed in subsequent reactions[68]:



(50)

The determination of the sequence of the dissociation of the C–C or one of the C–O bonds in the epoxy-ring under the influence of ultraviolet light constitutes a very complex problem, which requires solution and a theoretical treatment. The mode of photochemical decomposition of the epoxy-ring is determined by the electromeric effect of the ring substituents[89-91,93] and the degree of weakening of the bonds in the ring. Furthermore, account must be taken of the isomeric structure of the molecules[90,94,99] and the effect of reactive solvents, for example, acetone[72] or methanol, both on the reaction and the polarisation of the C–O bonds in the three-membered ring, which has been scarcely investigated. Different views have been expressed about the effect of methanol on the epoxy-group. In one case[103] such an effect was noted (a shift of the band due to the hydrogen bond in the infrared spectrum of the same order of magnitude as for the methanol–acyclic ether pair, namely 80–99 cm^{-1}), while in another case[104] such an effect was denied (the infrared spectra of mixtures of epoxyalkanes and alcohols failed to reveal any interaction between them). In a third communication[105] it is stated that the interaction of the hydroxy-group with the ring involves the electrons of the C–O bond and that it occurs when the hydroxy group approaches not the apex of the ring but its plane. Account must also be taken of the effect of the size of the incident quanta, the duration of the irradiation, and the sensitisers used. Although compounds 10 and 11 (Table 4) do not absorb light at wavelengths higher than 3000 Å, their irradiation with light at a wavelength of 2537 Å for only 5 s is sufficient to cause further photolysis on irradiation with light at a wavelength of 3500 Å, which suggests a sensitising effect by the photochemical decomposition products[100]. The introduction into the reaction medium of photosensitisers, for example benzophenone (a decomposition product of compound 11, Table 4), leads to an increase of the yield of diphenylcarbene compared with non-sensitised photolysis. Possibly the photosensitiser arising in the photochemical decomposition of epoxy-compounds facilitates the transition of diphenylcarbene as well as other carbenes to a triplet state, as in the formation of triplet methylene in the presence of benzophenone[106], and thereby influences the reaction.

V. RADICAL PROCESSES IN EPOXY-COMPOUNDS INDUCED BY HIGH-ENERGY RADIATION

The radiation-chemical reactions of epoxy-compounds are the least investigated branch of the chemistry of three-membered heterocycles. The explanation is that the radiolysis of epoxy-compounds began to be investigated only in recent years and the radiation processes are extremely complex, since they involve the simultaneous occurrence of reactions with participation of radicals, radical-ions, ions, etc. These factors make it difficult to elucidate the mechanisms of the radiation-chemical reactions of epoxy-compounds.

One of the first tasks undertaken in the study of radiation-induced reactions of epoxy-compounds consisted in the investigation of their polymerisation. For this purpose, epoxyethane was irradiated. However, it did not polymerise either in the liquid[107,108] or solid[109,110] phases or in methylene chloride solution[107]. A polymer was obtained in 0.22% yield by irradiating epoxyethane in the solid phase (dose 8 Mrad, dose rate 15.5 rad s^{-1}, −80°C, vacuum)[111]. By changing the irradiation conditions (41.6 Mrad, 50 rad s^{-1}, room temperature), the yield of the polymer was

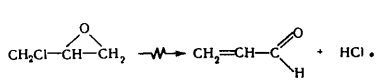
increased to 1.37%. The addition of inorganic oxides (ZnO, SiO_2, MgO, and As_2O_3) had little effect on the yield of the polymer.

Hoshino et al.[112] observed the formation of a polymer and acetaldehyde from epoxyethane and determined their yields. The gaseous products evolved were analysed. They concluded that the radiation-induced decomposition of epoxyethane involves both radical and molecular mechanisms, the polymerisation reaction predominating.

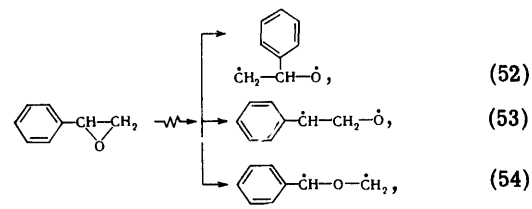
Frequent attempts to achieve the radiation-induced polymerisation of pure epoxypropane by a radical mechanism were unsuccessful[107,109,110,113-115]. Nevertheless the absence of a polymeric product in the irradiated epoxypropane cannot be regarded as proof that radical processes are impossible. An ESR study of the radiolysis of epoxypropane (between −140° and −170°C) established the formation of two types of radicals and their structure. Trofimov and Chkheidze[116] showed that the ESR spectrum of irradiated epoxypropane is produced by the superposition of a triplet with $\Delta H_T = 18$ Oe and the spectrum with a line width $\Delta H_{tot} = 82$ Oe. The glycidyl radical (XI) ($\Delta H_\alpha = 18.5$ Oe, $\Delta H_\beta = 0$) makes the main contribution with a small contribution by the epoxy-radical (VIII) (hyperfine structure splitting of 82 Oe). Radicals formed as a result of the opening of the three-membered ring were not detected.

Tabata[114] and Tabata and Sobue[117,118] described the synthesis of a homopolymer of epoxypropane in the liquid and solid phases mixed with epoxyethylbenzene. Whereas previously the authors considered the radiation-induced polymerisation of epoxypropane in the presence of epoxyethylbenzene from the standpoint of a radical mechanism, in their latest publication[115] they concluded that the process has an ionic mechanism (low activation energy, the absence of an effect by radical inhibitors).

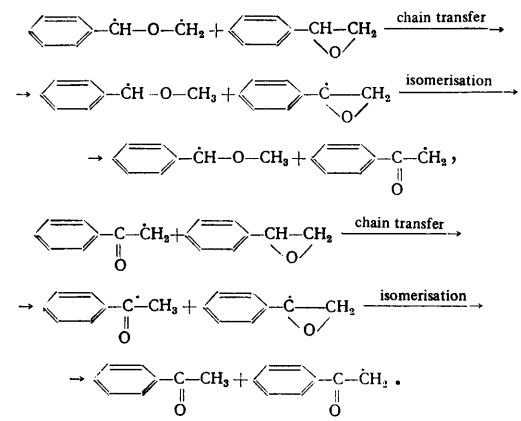
Radiation-induced polymerisation of epichlorohydrin (ECH) in the solid[110] and liquid states[119,120] was not observed. The infrared spectra of irradiated epichlorohydrin show new bands at 3450 cm^{-1} (hydroxy-groups) and 1720 cm^{-1} (carbonyl group) (cobalt-60 radiation, 400 Mrad). It has been noted[121] that the epoxy-ring is opened on radiolysis of epichlorohydrin with formation of carbonyl and hydroxy-groups and probably ether bonds (band with a maximum at 1065–1120 cm^{-1}). The viscosity of epichlorohydrin increases in the course of irradiation. Dichlorohydrin, acrolein and water (liquid phase) and hydrogen, methane, ethane, propane, and an unknown substance (gas phase) were detected among the radioysis products. One of the possible pathways in the formation of dichlorohydrin is as follows. H or Cl radicals are split off during the radiolysis and either recombine to HCl or abstract chlorine and hydrogen respectively from the epichlorohydrin molecule. Further reaction of hydrogen chloride with epichlorohydrin takes place by the familiar mechanism[122]. Acrolein may be formed from epichlorohydrin as a result of the elimination of hydrogen chloride:


(51)

Epoxyethylbenzene polymerises on cobalt-60 irradiation (8–54 rad s^{-1}) or irradiation with accelerated electrons (8×10^4–2×10^5 rad s^{-1}) at temperatures between −196° and 140°C in the solid and liquid phases[114,115,117]. The rate of radiation-induced polymerisation of epoxyethylbenzene and its conversion increase with temperature. The radiation-chemical yield at 140°C is $G_{-M} = 1000$. The overall activation energy for the liquid-phase process is 6.25 kcal $mole^{-1}$. An increase of the dose increases the yield of the polymer and the degree of polymerisation. Benzoquinone (2%, 20°C, dose rate 23.8 rad s^{-1}) inhibits the reaction over a period of 150 h. All these data support a radical chain mechanism of the radiation-induced polymerisation of epoxyethylbenzene. In their discussion of the process mechanism, the authors postulate the formation of three types of biradicals arising on dissociation of the principal bonds of the epoxy-ring:


(52) (53) (54)

and suggest that the reaction takes place simultaneously by several pathways. In one of these the interaction of the primary radical with the monomer is represented by the following mechanism taking into account repeated chain transfer (abstraction of hydrogen atoms) and isomerisation:


(55) (56)

The importance of the role of fast chain transfer and isomerisation reactions in this mechanism appears to be significantly responsible for the low rate of propagation and for the presence of stages in the reaction[118].

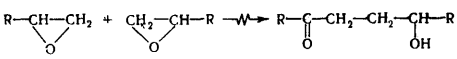
Colichman and Strong[123] did not observe any changes in an epoxy-resin after irradiation (cobalt-60, 100 Mrad, 55 rad s^{-1}, 38°C) and decided that radiation cannot promote the interaction in resins involving epoxy-groups. Nor was polymerisation observed after the irradiation of the pure diglycidyl ether of 2,2-di(*p*-hydroxyphenyl)propane[119].

On the other hand, it has been shown that epoxydian† resins (EDS) of types ED-5, ED-6, EDP, and EDL not only polymerise but are also cross-linked under the influence of high-energy radiation at room temperature without the use of hardening agents[124-128]. The study of the radiation-chemical reactions of these resins showed that the epoxy-group is the most sensitive unit in their molecule. The rate of decomposition of the epoxy-rings in the resins of all types was the same, being proportional to the dose both in a vacuum and in the presence of atmospheric oxygen. It is independent of the phase state (under the usual conditions, the ED-5 and ED-6 resins are liquid and EDP and EDL are solid) and the molecular weight of the resin in the range 370–1200, of the initial content of epoxy-groups in

† Dian = di(*p*-hydroxyphenyl)dimethylmethane (Ed. of Translation).

the resins (9–22%), and of the dose rate. The radiation-chemical yield of the reactions of the epoxy-groups proved to be 2.66 groups/100 eV. The rate of decomposition of epoxy-groups increases with temperature. The increase of the density, refractive index, and molecular weight varies linearly with the dose. These changes convincingly demonstrate the occurrence of radiation-induced polymerisation of unhardened epoxydian resins.

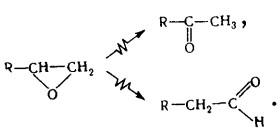
The nature of the radiation-chemical reactions of the epoxy-rings were inferred, in particular, from the changes in the infrared spectra. The intensity of the 915 cm^{-1} band (epoxy-groups) decreased, the band in the region of 3500 cm^{-1} became broader and more intense (hydroxy-groups and intermolecular hydrogen bonds), and a new band appeared at 1720 cm^{-1} (carbonyl groups). The formation of carbonyl groups and the increase of the concentration of hydroxy-groups cannot be attributed to radiation-induced oxidation reactions. There is a genetic relation between the decomposition of epoxy-groups and the formation of carbonyl groups and also the increase of the concentration of hydroxy-groups. Possibly it is revealed in the interaction of the epoxy-groups of two molecules of an epoxydian resin:



(57)

As already mentioned, the formation of carbonyl groups from epoxy-rings is evidence of the occurrence of radical processes.

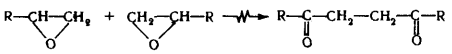
One of the causes of the low rate of radiation-induced polymerisation of the resin is intramolecular rearrangements, which in fact lead to the consumption of epoxy-groups but do not give rise to an increase of the molecular weight. Depending on the site of the homolytic cleavage of the ring, ketones and aldehydes may be formed:



(58)

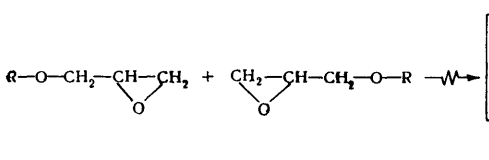
(59)

The formation of carbonyl groups, which is accompanied by the breakdown of epoxy-groups and a linear increase in the length of the resin molecules, can also occur as a result of the following reaction:



(60)

The radiation-chemical yield of the total gaseous product is smaller by a factor of almost 36 than the decomposition yield of the epoxy-groups and amounts to 0.074 mol./100 eV. The gaseous mixture consists mainly of hydrogen, but since $(G_{\text{-ep.gr.}}/2)/G_{\text{gas}} \ll 1$, reaction (60) occurs relatively rarely even if it is assumed that it is the sole source of hydrogen.

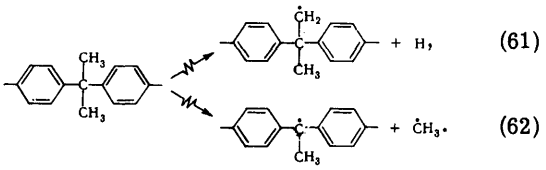


(64)

(65)

Polyfunctional epoxy-compounds the molecules of which contain, in addition to epoxy-rings, various other reactive groups, for example, double bonds are of definite interest. Glycidyl methacrylate (GMA) polymerise in the solid state

The molecular-structural changes in solid epoxydian resins were investigated by Bakaeva et al.[120] (cobalt-60, 1500 Mrad, 84–2100 rad s^{-1}).[120] In view of the similarity of the ESR spectra of irradiated 2,2-di(*p*-hydroxyphenyl)-propane and the resin, the authors believe that the primary radiation-chemical steps in the resins are the following radical reactions:

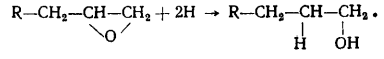


(61)

(62)

As assumed by Bakaeva et al.[120], the formation of bonds between resin molecules occurs only as a result of the interaction between radicals formed by reactions (61) and (62). However, such a reaction is complicated by the rigidity of the *p*-phenylene unit[129,130] and of the entire resin molecule[126], i.e. a sharp decrease in mobility and greater inhibition of the rotation of all the units of the molecular chain, when the resin solidifies[131]. Furthermore, a change in the type of substituent or an increase in the length of the side chain at the central dian atom might lead to a change in the ultraviolet spectrum of the compound when the concentration of new bonds is sufficiently high[132]. However, after irradiation with a dose of 500 Mrad the ultraviolet spectra of the resins proved to be identical with those of the non-irradiated resins. This indicates, firstly, a low probability of the reactions of the above radicals with one another, secondly, the absence of reactions involving addition to the benzene ring in the *o*- and *m*-positions, and, thirdly, the high radiation stability of the bond between the quaternary carbon atom and the phenyl rings in the resin molecules[128].

Like Colichman and Strong[123], Bakaeva et al.[120] do not postulate a linear growth of the resin molecules and the participation of the epoxy-groups in this process. They believe[120] that the epoxy-groups decompose by reaction (58) or form a primary alcohol as a result of hydrogenation:



(63)

The radiation-chemical reactions of the diglycidyl ether of ethylene glycol (DEG) obey very largely the same relations as the reactions of epoxydian resins[125,127,128]. The absence of aromatic rings from DEG favours more vigorous gas evolution ($G_{\text{gas}} = 0.95$ mol./100 eV) and decomposition of epoxy-groups ($G_{\text{-ep.gr.}} = 5.66$ groups/100 eV). On the basis of chemical analyses and ultraviolet and infrared spectra, it has been suggested that, on irradiation of DEG, the enol of a β-diketone is formed apart from the occurrence of reaction (57):

(cobalt-60, 0.4 Mrad, 3–600 rad s^{-1}) by a radical chain reaction with bimolecular chain termination[133]. After 10–15% conversion, a gel fraction is formed. The appearance of a three-dimensional structure is regarded as proof of

the involvement in the reaction of both functional groups, since it is well known that monofunctional monomers, for example, methyl methacrylate and butyl methacrylate (the closest analogues of GMA) are degraded and not cross-linked by radiation. In the initial stage of the process the polymerisation of GMA involves mainly the double bonds. But even in this stage the epoxy-groups are involved also.

The data presented show that, under the action of high-energy radiation, radical processes occur in epoxy-compounds as a result of which they can polymerise via the epoxy-groups, isomerise to carbonyl compounds, and give rise to ethers and hydroxy-groups. Despite some analogy with the double bond[134], the three-membered epoxy-ring is much less reactive.

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The data presented show that under certain conditions epoxy-compounds may react by a radical mechanism. Despite the various methods of initiation of the radical reactions of epoxy-compounds, the results are the same in most cases—cleavage of the C–O bond of the ring. The site of the dissociation of the bond is little affected by the form of activation: nuclear vibrations (pyrolysis), electron excitation (photochemistry), radical attack (chemical initiation), and radiation-induced reactions. The electronic structure of their molecules plays a decisive role in the mode and rate of the reactions of epoxy-compounds. It is reasonable to expect that the epoxy-ring may be cleaved at different sites, since the strength of the bonds in it depends on the substituents. Consequently one of the most important tasks in the study of the mechanism of the radical processes involving epoxy-compounds is the identification of the intermediate products in order to establish the site of the dissociation of the chemical bonds in the epoxy-ring and the effect on the cleavage of the number and nature of the substituents at the ring carbon atoms.

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