Reports of the Academy of Sciences of the USSR

Yu. N. MOLIN, I. I. CHKHEIDZE, A. A. PETROV, N. Ya. BUBEN

1960

SovietRxiv

Abstract

Full Text

Reports of the Academy of Sciences of the USSR
1960. Volume 131, No. 1

PHYSICAL CHEMISTRY

Yu. N. MOLIN, I. I. CHKHEIDZE, A. A. PETROV, N. Ya. BUBEN
and Corresponding Member of the Academy of Sciences of the USSR V. V. VOEVODSKII

STUDY OF ENERGY-TRANSFER PROCESSES IN THE RADIOLYSIS OF CERTAIN FROZEN HYDROCARBONS BY THE E.P.R. METHOD

The rupture of a chemical bond during the radiolysis of organic compounds in the condensed phase may be preceded by intramolecular and intermolecular transfer of energy over considerable distances. A large number of studies have been devoted to consideration of this question, in which conclusions about energy transfer are drawn both on the basis of chemical analysis of the final products (see, for example, (^{1})) and on the basis of physical, for example spectroscopic, measurements (^{2}). Substantially new possibilities for investigating energy-transfer processes are opened up by the use of the electron paramagnetic resonance method (e.p.r.), which makes it possible to record the primary act of chemical-bond rupture and radical formation, uncomplicated by secondary chemical processes.

In the present work, energy transfer was investigated during the radiolysis of frozen compounds I—III, listed in Table 1. Two approaches were used to study energy transfer. First, since the e.p.r. spectra of the simplest hydrocarbons—benzene (^{3}), cyclohexane (^{4}), and linear paraffins ($^{4-6}$)—irradiated in the frozen state have been well studied, it is possible, from the form of the e.p.r. spectrum, to determine the site of chemical-bond rupture in the complex molecules I—III and thus to follow the transfer of energy. Second, energy transfer to the aromatic ring should appear as a decrease in the total radiation yield of radicals, because aromatic rings in complex molecules exert a protective effect during radiolysis (^{7}).

Table 1

Compound	G, rad/100 eV
I. 1,1-Dicyclohexyldodecane[[structural formula: two cyclohexyl rings attached to $CH{-}C_{11}H_{23}$]]	4.9
II. 1,1-Diphenyldodecane[[structural formula: two phenyl rings attached to $CH{-}C_{11}H_{23}$]]	0.42
III. 1-Phenyl-1-cyclohexyldodecane[[structural formula: phenyl ring and cyclohexyl ring attached to $CH{-}C_{11}H_{23}$]]	0.46
Mixture I and II(1 : 1 by volume)	0.73
Cyclohexane[[structural formula: cyclohexane ring]]	1.6
Benzene[[structural formula: benzene ring]]	0.16

Proceeding from these considerations, we recorded the e.p.r. spectra of compounds I—III, benzene, and cyclohexane, irradiated with fast electrons (1.6 MeV) at −120°, and investigated the kinetics of radical accumulation. Along with the individual compounds, a mixture of compounds I and II was also studied. The measurements were carried out on an apparatus that made it possible to record e.p.r. spectra during irradiation with fast electrons (8). The measurement procedure was described in detail earlier (9); the synthesis and physicochemical properties

compounds I-III were described in work (10). Benzene and cyclohexane were chemically pure. The EPR spectra of the compounds studied (in the form of first derivatives of the absorption lines), recorded at a frequency of ~ 9400 MHz, are shown in Figs. 1 and 2.

The spectrum of compound I contains the same lines and has the same parity as the spectrum of irradiated cyclohexane, which is produced by the cyclohexyl radical C_6H_{11} (4). Thus, upon irradiation of compound I, radicals of the cyclohexyl type are formed in considerable amounts. The worsening of the resolution of the hyperfine structure of the EPR spectrum on going from cyclohexane to compound I can be explained by superposition of the spectra of isomeric radicals of the general formula RC_6H_{10}. It should be noted, however, that in the spectrum of compound I there are additional lines (marked by arrows) lying outside the spectrum of the cyclohexyl radical; these, apparently, should be ascribed to radicals formed upon rupture of a C—H bond in the linear chain of molecule I.

Fig. 1. EPR spectra of irradiated: a—cyclohexane, b—I (−120°)

Figure 1: Fig. 1. EPR spectra of irradiated: a—cyclohexane, b—I (−120°)

Fig. 2. EPR spectra of irradiated: a—benzene, b—II, c—III, d—mixture of I and II, 1:1 by volume (−120°)

Figure 2: Fig. 2. EPR spectra of irradiated: a—benzene, b—II, c—III, d—mixture of I and II, 1:1 by volume (−120°)

It is known (4-6) that the EPR spectra of radicals of linear hydrocarbons have a width of the order of 150-160 Oe. Thus, in the case of compound

Fig. 1. EPR spectra of irradiated:
a —cyclohexane, *b* —I (−120°)

Fig. 2. EPR spectra of irradiated:
a —benzene, *b* —II, *c* —III, *d* —mixture of I and II, $1:1$ by volume (−120°)

I radicals are formed corresponding to rupture of a C—H bond both in the ring and in the linear chain.

The spectra of irradiated compounds II and III are identical and analogous to the spectrum of irradiated benzene. This means that, in the case of compounds II and III, as in the case of benzene (3), radicals of only two types are formed —one by abstraction of an H atom from the benzene ring and the other by addition of an H atom to the benzene ring. The absence of additional hyperfine structure in compounds II and III, and the somewhat poorer resolution of the components of the main triplet compared with benzene, is evidently associated with the absence of internal rotation (3). It is very significant that in the spectra of the compounds studied there are no lines corresponding to rupture of C—H bonds in the linear chain (II and III) and in the cyclohexyl ring (III). In the case of a mixture of compounds I and II, the EPR spectrum is close to the spectrum of compound II. The somewhat poorer resolution of the spectrum of the mixture and the presence

the additional shoulders (marked by arrows) can be explained by the superposition of a small admixture of the spectrum of compound I. Thus, upon irradiation of the mixture, radicals are formed predominantly on molecules II.

The analysis of the spectra shows that in molecules II and III the primary rupture of the chemical bond occurs only in the benzene ring. Consequently, the energy received by the different groups of molecules II and III has time, before the chemical bond is broken, to be redistributed and to pass into the benzene ring. In the case of a mixture of compounds I and II, this intramolecular energy transfer is accompanied by the transfer of energy from molecules I to molecules II. The complex character of the spectrum in the case of compound I does not make it possible to establish whether directed intramolecular energy transfer occurs.

Fig. 3. Kinetics of radical accumulation (−120°). 1 –I, 2 –cyclohexane, 3 –mixture of I and II 1:1 (by volume), 4 –III, 5 –II, 6 –benzene

Figure 3: Fig. 3. Kinetics of radical accumulation (−120°). 1 –I, 2 –cyclohexane, 3 –mixture of I and II 1:1 (by volume), 4 –III, 5 –II, 6 –benzene

The initial portions of the radical-accumulation curves are presented in Fig. 3. In compounds containing benzene rings, up to a dose of 100 Mrad no deviation from the linear law of accumulation is observed. In compound I and in cyclohexane, linearity is already disrupted at doses of 10–30 Mrad. The radiation yields of radicals G_R, found from the initial linear portions of the accumulation curves, are given in Table 1. It should first of all be noted that in compounds II and III, which contain benzene rings, the yield of radicals is an order of magnitude smaller than in compound I. This result confirms the conclusion, made on the basis of spectral analysis, concerning the transfer of energy into the benzene ring. In the absence of such transfer, and with independent formation of radicals on different parts of the molecule, the radical yields in the case of compounds II and III should have been close to the yield in the case of compound I, since the electronic fraction of the saturated groups in molecules II and III is approximately 50 and 75%, respectively. Energy transfer into the benzene ring makes it possible to explain the practically identical value of the radical yield for molecules II and III. The energy received by these molecules is completely concentrated in the benzene ring, and the radical yield is determined only by the stability of the ring.

Fig. 3. Kinetics of radical accumulation (−120°). 1 –I, 2 –cyclohexane, 3 –mixture of I and II 1:1 (by volume), 4 –III, 5 –II, 6 –benzene

The low value of the radiation yield for the mixture of compounds I and II is convincing confirmation of the conclusion about energy transfer from I to II. In the absence of interaction between the components of the mixture, the radical yield should have been $\gamma_I G_I + \gamma_{II} G_{II} \simeq 2.5$, which is considerably higher than that found experimentally (γ_I and γ_{II} are the electronic fractions of molecules I and II in the mixture). At the same time it should be noted that the radiation yield in the mixture proved to be somewhat greater than in the case of compound II. This result, as well as the poorer resolution of the spectrum of the mixture, indicates that not all the energy received by molecules I has time, before the act of chemical-bond rupture, to pass to molecules II. If it is assumed that the increase in G_R in the mixture is entirely due to the formation of radicals from molecules I, then it can be shown that about 10% of the molecules I do not have time to transfer their

energy. It is possible that this is connected with the insufficient efficiency of intermolecular energy transfer. It is not excluded, however, that the frozen mixture of I and II is insufficiently homogeneous, which may also hinder the transfer of energy to molecules of II.

It should be noted that the radiation yields of radicals in compounds II and III are almost three times greater than the yield of radicals in benzene. The decrease in the radiation resistance of a molecule upon introduction of an alkyl substituent into the benzene ring is a well-known fact ([11]); however, this decrease is usually associated with the possibility of bond rupture in the side chains. Since, as follows from analysis of the EPR spectra, in the radiolysis of compounds II and III radicals are formed as a result of rupture of C—H bonds only in the benzene ring, the indicated difference in radical yields may be ascribed to a decrease in the stability of the benzene ring upon introduction of a substituent into it.

In conclusion, the authors express their gratitude to G. K. Voronova for assistance in carrying out the experiments and in processing the measurement results.

Institute of Chemical Kinetics and Combustion
Siberian Branch of the Academy of Sciences of the USSR

Institute of Chemical Physics,
Institute of Geology and Development of Mineral Resources
Academy of Sciences of the USSR

Received
4 XI 1959

CITED LITERATURE

[1] J. P. Manion, M. Burton, *J. Phys. Chem.*, **56**, 560 (1952).
[2] H. T. J. Chilton, G. Porter, *J. Phys. Chem.*, **63**, 904 (1959).
[3] I. I. Chkheidze, Yu. N. Molin et al., *DAN*, **130**, No. 6 (1960).
[4] N. Ya. Chernyak, N. N. Bubnov et al., *Optics and Spectroscopy*, **6**, 564 (1959).
[5] B. Smaller, M. S. Matheson, *J. Chem. Phys.*, **28**, 1169 (1958).
[6] R. S. Alger, T. H. Anderson, L. A. Webb, *J. Chem. Phys.*, **30**, 695 (1959).
[7] L. T. Bugaenko, T. S. Nikitina et al., *Chemical Action of Ionizing Radiations*, Moscow, 1958.
[8] Yu. N. Molin, A. T. Koritskii et al., *DAN*, **123**, 882 (1958).
[9] A. T. Koritskii, Yu. N. Molin et al., *High-Molecular Compounds*, **1**, 1182 (1959).
[10] S. R. Sergeenko, L. N. Kvitkovskii et al., *DAN*, **120**, 541 (1958).
[11] M. Burton, S. Gordon, R. R. Hentz, *J. Chim. Phys.*, **48**, 190 (1951).

Note: Figure translations are in progress. See original paper for figures.