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E. B. Milovskaya, B. L. Erusalimskii, and B. A. Dolgoplosk

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Abstract

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E. B. Milovskaya, B. L. Erusalimskii, and B. A. Dolgoplosk

Reactions of Free Radicals in Solutions

Interaction of Free Radicals with Internal and External Double Bonds

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As was shown in (^{1}), double bonds of the vinyl type are effective acceptors of free radicals. In the present work, data are presented that characterize the relative activity of internal and external double bonds in the reaction of interaction with free radicals.

Interaction of the methyl free radical with hydrocarbons and polymers. As a source of methyl free radicals we used methylphenyltriazene, which decomposes on heating in solution according to the equation:

$$CH_3N{=}N{-}NHC_6H_5 \rightarrow CH_3\cdot + N_2 + \cdot NHC_6H_5. \quad (1)$$

The degree of interaction of free radicals with double bonds was assessed indirectly from the decrease in the yield of methane formed by the reaction:

$$R\cdot + LH \rightarrow RH + L\cdot \quad (2)$$

(LH is a hydrocarbon molecule), in comparison with the yield of CH_4 observed when the process is carried out in a saturated hydrocarbon medium. The results obtained show that an internal double bond is considerably less capable of adding free radicals than a double bond of the vinyl type. The same conclusion was led to by data obtained in studying the interaction of methyl free radicals with polymers (see Table 1). In this case the reaction was carried out in concentrated isopropylbenzene solutions, with a solution of polystyrene of the corresponding concentration used as the standard. The practical coincidence of the values for polystyrene and natural rubber makes it possible to assume that addition of free radicals to the double bonds of the latter proceeds to an insignificant extent. By contrast, for synthetic polyisoprene with a high content of vinyl double bonds, a sharp decrease in the methane yield is observed.

We have established that in swollen polystyrene containing 10% isopropylbenzene, the methane yield is only 9%, whereas in pure isopropylbenzene this value is 49% of theory. The decrease in methane yield on going to highly viscous media is due to the increasing role of primary recombination of the free radicals formed according to reaction (1). This is confirmed by the fact that the yield of methylaniline (the product of primary recombination) in a pure solvent is 16%, while in swollen polystyrene it is 43%. This also explains the decrease in methane yield during the decomposition of triazene in concentrated solutions of rubbers.

Table 1

Methane yield during the thermal decomposition of methylphenyltriazene in various hydrocarbons (concn. of triazene 3 mol. %) and in polymers containing 34% isopropylbenzene (concn. of triazene 15 wt. % relative to polymer). Temperature 110°

Hydrocarbons	Yield of CH_4, % of theory	Polymers	Yield of CH_4, % of theory
n-Butane	54	Polystyrene	29
1-Heptene *	12	Natural rubber	27
Isobutylene	8	Polyisoprene containing up to 70% of units 1, 2 and 3, 4	14
α-Methylstyrene *	0		
2-Butene	30		

* Data reported in the preceding communication (1) were obtained at other temperatures and concentrations.

Thus, the transition to highly viscous media leads to a decrease in the fraction of effective radical reactions.

Interaction of the dimethylcyanomethyl free radical with 2-butene. To generate dimethylcyanomethyl free radicals, the dinitrile of azoisobutyric acid was used. Data on the compounds detected in the products of thermal decomposition of the dinitrile of azoisobutyric acid in 2-butene are summarized in Table 2.

Table 2

Yield of transformation products of the dimethylcyanomethyl free radical in a butene medium, in % of theory. Temperature 80°. Concentration of azo compound 5 mol. %

R–R	RH	RAR	$RA_{(+H)} + RA_{(-H)}$
79	3	3.5	2

(R –radical, A –hydrocarbon molecule).

From these data it follows that addition of dimethylcyanomethyl free radicals to an internal double bond proceeds to a very slight extent. Under the conditions of the experiments carried out, the indicated radicals predominantly recombine. Under analogous conditions, as we showed earlier (^{1}), for hydrocarbons containing a vinyl group, the principal reaction is addition of free radicals to the double bond. The free radicals $RA\cdot$, formed as a result of interaction of the primary radicals $R\cdot$ with 2-butene, are distinguished by low reactivity. This follows from the nature of the products of their further transformation, whose formation corresponds to the scheme:

$$RA\cdot \begin{cases} \xrightarrow{R\cdot} RAR \\ \xrightarrow{RA\cdot} RA_{+H} + RA_{-H}. \end{cases} \tag{3}$$

$$\tag{4}$$

The compound RAR should be assigned the structure of the dinitrile of 2,2′,3,4,5,5′-hexamethyladipic acid. The products of disproportionation of radicals $RA\cdot$ (reaction (4)), which could not be separated into individual compounds, were characterized as an equimolecular mixture of saturated and unsaturated components. The formation of the nitrile of isobutyric acid (RH), with the same yield as when carrying out the reaction in other hydrocarbons (^{1}), apparently is the result of disproportionation of the primary free radicals.

Experimental Part

Decomposition of methylphenyltriazene in various media. Experiments with low-boiling hydrocarbons were carried out in a small autoclave with an average charge of 1 g of triazene (concn. 3 mol. %). Experiments with polymers were carried out in ampoules equipped with a tube and outlet connected to a gas burette. After the decomposition was completed (8 h at 110°), water was introduced through the tube, and the contents of the ampoule were sparged until the gas "trapped" in the polymer ceased to be evolved. For an experiment, 2 g of polymer was taken; the ratio of all components is given in Table 1.

Determination of the yield of methylaniline upon decomposition of triazene in isopropylbenzene and in swollen polystyrene was carried out by successive use of the bromide-bromate method and the express method of Shchetinina[^2].

Decomposition products of azoisobutyric acid dinitrile in 2-butene. 20 g of the dinitrile was decomposed in an autoclave in 135 g of 2-butene at 80°. After distillation of the butene that had not entered into reaction, the following products were isolated:

a) Tetramethylsuccinic acid dinitrile, 13 g (yield 79% of theory), m.p. 168–168.5°; lit. 169°[^3]. Mixed sample 168.5°.

b) Isobutyric acid nitrile, 0.64 g (yield 3% of theory), determined by saponification of the toluene fraction obtained on distillation of toluene previously introduced into the reaction mixture, freed from 2-butene and from the bulk of the tetramethylsuccinic acid dinitrile; the latter compound, under the conditions of the method used, is not saponified[^4].

c) Fraction b.p. 25–26°/0.5 mm. Yield 0.7 g (2% of theory), $d_4^{19.5}$ 0.8123; $n_D^{19.5}$ 1.4248.

Found, %: N 11.19; 11.39; M 118.5. Iodine number 102
$C_8H_{15}N$(RAH). Calculated, %: N 11.20; M 125. Iodine number 0
$C_8H_{13}N$(RA(−H)). Calculated, %: N 11.38; M 123. Iodine number 206.

d) Fraction b.p. 102–105°/0.5 mm. d_4^{20} 0.9250; n_D^{20} 1.4620. Yield 0.85 g (3.5% of theory).

Found, %: C 74.27; 74.35; H 10.27; 10.30; N 14.34; 14.45; M 187.5; MR 57.24
$C_{12}H_{20}N_2$(RAR). Calculated, %: C 75.00; H 10.41; N 14.58; M 192; MR 57.07

e) Resinous non-distilling residue, 1.5 g.

Found, %: N 15.41; M 232.

The content of bound dimethylcyanomethyl radicals (by % nitrogen) was 6.5% of the initial amount.

Institute of High-Molecular Compounds
Academy of Sciences of the USSR

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References

1. E. B. Milovskaya, B. A. Dolgoplosk, B. L. Erusalimskii, *Izv. AN SSSR, OKhN*, **1957**, 494.

2. R. P. Lastovskii, *Technical Analysis in the Production of Intermediates and Dyes*, 1949, pp. 166, 212.

3. F. K. Beilstein, *Handbuch der organischen Chemie*, **2**, p. 707.

4. P. Bruin, A. F. Bickel, E. C. Kooyman, *Rec. Trav. Chim.*, **71**, 1115 (1952).