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Abstract

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FORMATION OF FREE RADICALS

IN BIMOLECULAR REACTIONS

THE REACTION BETWEEN TRIPHENYLCHLOROMETHANE AND ETHYLLITHIUM

(Presented by Academician V. N. Kondrat' ev on 16 VII 1958)

In 1954 N. N. Semenov (^{1}) proposed the hypothesis that the activation energy of an elementary reaction of two molecules with formation of free radicals

$$\mathrm{R'X + YR'' \rightarrow R'\cdot + XY + \cdot R''} \tag{1}$$

is determined mainly by the endothermicity of the process, whereas the activation barrier of such reactions should be small. Consequently, if compounds are chosen in which the sum of the energies of the bonds being broken, R′—X and R″—Y, does not considerably exceed the energy of the bond X—Y being formed, or is even less than it (i.e., process (1) is close to thermoneutral or exothermic), then the reaction between these compounds should proceed with a small activation energy. This condition is satisfied by the interaction of alkyl halides with organometallic compounds, which occurs, in particular, in the widely known reactions of Wurtz, Fittig, and Grignard. The mechanism of these reactions, however, is far from clear. Ziegler, Ochs, Hoffmann, and Jilman ($^{2-4}$), who studied the reactions of organometallic compounds with alkyl halides, assumed in some cases the occurrence of radicals, but the paths of their formation remained unexplained.

We studied the interaction of triphenylchloromethane with ethyllithium, the first step of which, if it proceeds according to scheme (1),

$$\mathrm{(C_6H_5)_3CCl + {}'LiC_2H_5 \rightarrow (C_6H_5)_3C\cdot + LiCl + C_2H_5}, \tag{2}$$

should apparently be exothermic*. The relatively low rate of dimerization of triphenylmethyl radicals (^{7}), formed in the course of the reaction, made it possi-

Fig. 1

Figure 1: Fig. 1

ble to use the method of electron paramagnetic resonance for identifying these radicals and determining their concentration during the course of the process. The reaction was carried out in a thin-walled test tube placed in the resonator of an EPR spectrometer. Toluene solutions of the reagents, separated by a membrane, were mixed by breaking it with a thin glass rod. In the course of the reaction, EPR indeed detected radicals whose hyperfine-structure spectrum, shown in Fig. 1, corresponded exactly to the absorption spectrum of triphenylmethyl radicals recorded earlier (^{8}).

Figure 2 gives kinetic curves for the change in concentration of triphenylmethyl radicals during the reaction at −44, −54, and −80°. It is seen that the concentration of free radicals at the first moment of the reaction passes, at all temperatures, through a sharply expressed maximum and then falls. The descending branch of the curves represents recombination of the formed— of the triphenylmethyl radicals formed in the first step to their equilibrium concentration ($2(C_6H_5)_3C\cdot \rightleftarrows (C_6H_5)_3C—C(C_6H_5)_3$), which at the temperatures of the experiment is insignificant. The formation, at the very first moment of the reaction, of triphenylmethyl radicals in concentrations many times exceeding the equilibrium ones unambiguously indicates their primary formation. Indeed, if the triphenylmethyl radicals were formed upon dissociation of hexaphenylethane, produced primarily by some other route, then we would observe a slow increase in the concentration of radicals up to their equilibrium value. Special experiments established that the presence of a maximum on the kinetic curves is not associated with an increase in the temperature of the reaction mixture leading to dissociation of hexaphenylethane, since heating under the experimental conditions was insignificant.

Fig. 1

The nature of the kinetic curves in Fig. 2 corresponds to the accumulation of an intermediate product in consecutive bimolecular reactions. Using formulas obtained in calculating the kinetics of reactions of this type (^{9}), and taking into account the rate constants for dimerization of triphenylmethyl radicals (^{7}), from the kinetic curves obtained one can calculate the values of the rate constant and activation energy of the radical-formation reaction. Although, in doing so, errors associated with the very high rate of the first reaction (close to the rate of mixing of the reagents) cannot be avoided, the calculation leads to the definite

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* Indeed, $D(\mathrm{C—Cl})$ in $(\mathrm{C_6H_5})_3\mathrm{CCl}$ is 48 kcal (^{5}), $D(\mathrm{LiCl}) = 115$ kcal (^{6}). Then the heat of reaction (2) is $q = 115 - 48 - D(\mathrm{Li—C_2H_5}) = 67 - D(\mathrm{Li—C_2H_5})$. If, as may be thought, $D(\mathrm{Li—C_2H_5}) < 67$ kcal, then $q > 0$.

Fig. 2

Figure 2: Fig. 2

conclusion that the activation energy of the first reaction does not exceed 4–5 kcal. Thus, it may be considered proven that elementary reactions of type (1), under suitable energetic conditions, can proceed with the formation of free radicals with insignificant activation energy.

Fig. 2

Of particular interest is the fate of the ethyl radicals, whose formation follows from scheme (2). As is evident from Table 1, the only gaseous products of the reaction are ethane and ethylene, which would seem to indicate disproportionation of ethyl radicals. However, the presence of ethyl radicals in the reaction mixture could not be detected by any chemical methods. It is known that ethyl radicals formed in solution, at temperatures close to room temperature, abstract a hydrogen atom from the hydrocarbon solvent with formation of ethane. In solutions of aromatic hydrocarbons, ethyl radicals add to the solvent molecules, and the amount of ethane decreases (^{10}). If, under the selected conditions, disproportionation of ethyl radicals takes place, then simultaneously, and even at a higher rate, their recombination with formation of butane should occur (^{12}). In our experiments, when the reaction was carried out in solvents labeled with deuterium $(C_6D_6,\ C_6H_5CH_2D)$

the ethane formed proved to be light (mass-spectrometric analysis). The amount of ethane evolved proved to be the same when the reaction was carried out in decalin, toluene, benzene, and in benzene with added anthracene. These facts, as well as the absence of butane among the reaction products, force one

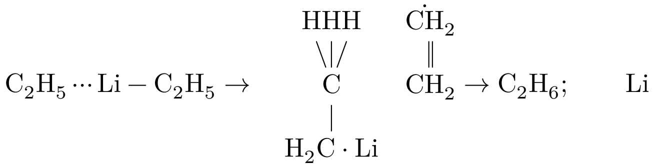
Table 1

Solvent	Reagents, mol • 10^4: C_2H_5Li	Reagents, mol • 10^4: $(C_6H_5)_3CCl$	Products, mol • 10^4: C_2H_4	Products, mol • 10^4: C_2H_6	Products, mol • 10^4: $(C_6H_5)_6C_2$	$[C_2H_4]/[C_2H_6]$
Benzene	9,33	8,0	0,55	1,85		0,3
Benzene	10,5	4,0	0,36	1,10		0,32
Benzene	10,5	2,0	0,13	0,60		0,22
Benzene	12,6	24,90	1,23	3,00		0,41
Benzene	12,6	12,6	1,12	2,70	1,4	0,41
Benzene	12,6	11,6	1,02	2,44		0,42
Benzene	21,4	18,5	1,68	6,03		0,28
Benzene	21,4	18,5	1,40	5,83		0,24
Decalin	10,1	5,1	0,22	0,75		0,29
Decalin	6,1	8,5	0,20	0,64	0,4	0,31
Decalin	8,1	8,2	0,23	0,90	0,43	0,25
Decalin	21,3	10,0	0,56	1,85		0,30

Solvent	Reagents, mol • 10^4: C_2H_5Li	Reagents, mol • 10^4: $(C_6H_5)_3CCl$	Products, mol • 10^4: C_2H_4	Products, mol • 10^4: C_2H_6	Products, mol • 10^4: $(C_6H_5)_6C_2$	$[C_2H_4]/[C_2H_6]$
Decalin	10,5	20,0	0,60	1,80	1,0	0,33
Decalin	21,3	20,0	1,55	3,05		0,38
Decalin	6,2	20,0	0,22	0,70		0,31
Decalin	18,0	21,1	0,86	2,53		0,34
Decalin	18,0	21,1	0,90	3,10	1,6	0,29

to conclude that free ethyl radicals are not formed in solution in the reaction under study. An explanation for this may be sought in the fact that, as was recently shown $(^{11})$, molecules of lithium alkyls in solutions form complexes with one another at the expense of the so-called lithium bond. It is possible that the ethyl radical formed in the course of the reaction remains bound in the complex and reacts with formation only of ethane and ethylene. The following hypothetical scheme may be proposed:

$$(C_6H_5)_3CCl + LiC_2H_5\cdots LiC_2H_5 \rightarrow (C_6H_5)_3C\cdot -LiCl + C_2H_5\cdots Li-\dot{C}_2H_5;$$



$$C_2H_5\cdots Li-C_2H_5 \rightarrow \begin{array}{c} HHH \\ \backslash|/ \\ C \\ | \\ H_2C\cdot Li \end{array} \quad \begin{array}{c} \dot{C}H_2 \\ \| \\ CH_2 \end{array} \rightarrow C_2H_6; \qquad Li$$

$$Li + (C_6H_5)_3CCl \rightarrow LiCl + (C_6H_5)_3C\cdot$$

The larger amount of ethane compared with ethylene may possibly be connected with side reactions of ethyllithium with the products of the primary reaction. Indeed, it was found that ethyllithium readily reacts with separately prepared triphenylmethyl radicals with evolution of ethane (apparently, a metalation reaction). In addition, it was shown that when the reaction of triphenylchloromethane with ethyllithium is carried out in the presence of ethylene added beforehand, partial absorption of the latter occurs, which may also affect the ratio of ethane to ethylene.

From the results presented in Table 1 it follows that only a certain fraction (approximately 20%) of the triphenylmethyl radicals forms hexaphenylethane. The remaining radicals apparently interact with ethyl radicals (possibly in the cage), forming products of their combination and disproportionation $[(C_6H_5)_3C{-}C_2H_5,\ (C_6H_5)_3CH,\ C_2H_4]$.

We do not consider it possible at present to extend the result obtained on the formation of radicals in the reaction under study to all reactions of haloalkyls with organometallic compounds. It is not excluded that in some cases a molecular or heteroly-

tic mechanism of the process. However, it must be taken into account that the absence of radicals in solution in such processes, for which there are some indications, may be explained by the disappearance of radicals through reactions in the solvent cage (dimerization and disproportionation) or through their intracomplex reaction, in the same way as we suppose this to occur for the ethyl radical.

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