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ELECTRON TRANSFER AS THE FIRST STEP IN NUCLEOPHILIC SUBSTITUTION

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A number of definitely useful formulations of theoretical organic chemistry which were advanced in the first half of the century are presently too rigid. For example, attempts at absolute classification of homo- and heterolytic reactions ignore the fact that heterolytic processes are frequently accompanied by free radical formation, while, on the other hand, homolytic reactions can lead to generation of ions. These phenomena are explained by assuming that homo- and heterolytic reactions both take place simultaneously and independently. It may be proposed, however, that one-electron transfer precedes the formation of the chemical bond in the transition state and is the first step of heterolytic as well as homolytic reactions.

The fact that a great variety of organic and inorganic species (metals[1], organometallic compounds[2], anions[3], Lewis bases[4], etc.) are capable of electron transfer is now evident. Carbonium ions[5], aromatic hydrocarbons, and molecules containing electronegative substituents[6] are also known to accept unpaired electrons with the formation of radicals or anion-radicals.

The intermediate formation of radical species cannot be excluded even in the case of heterolytic reactions but these species are not usually identified and their role in the course of reaction remains vague. There is some evidence that addition of Grignard reagents to benzophenone proceeds via ketyl formation[7]. Anion-radicals were also detected by ESR in the course of some metalation reactions[8,9] and in the reaction between 2-nitropropyl anion and p-nitrobenzyl bromide[10]. The interaction of triphenylchloromethane and ethyllithium is accompanied by the formation of free triphenylmethyl radicals[11].

In the case when an anion A^- reacts with cation B^+, it is possible that two radicals are originally formed:

$$A^{-} + B^{+} \longrightarrow A^{\bullet} + B^{\bullet} \qquad (1)$$

$$A^{\bullet} + B^{\bullet} \longrightarrow A\text{—}B \qquad (2)$$

Disproportionation and combination of like radicals results in the formation of by-products (A-A, AH, A_{-H}, etc.). If the electron transfer rate (1) is markedly in excess of that of recombination (2) the stationary concentration of free radicals may become measureable by the ESR method.

Typical examples of heterolytic processes are the hydrolysis and alcoholysis of alkyl halides. These reactions were the foundation of the generally accepted theory of nucleophilic substitution. From this point of view we believed it would be especially of interest to find electron transfer in such classic systems.

The system Ph_3CClO_4 + t-BuOK was used as a model on account of the fact that triphenylmethyl cation is a good electron acceptor and t-BuO-anion is a strong electron donor. This reaction turned out to occur in two steps, the first being the formation of triphenylmethyl radicals which are well detected by the ESR method:

$$Ph_3C^{+}ClO_4^{-} + t\text{-}BuOK \longrightarrow Ph_3C^{\bullet} + t\text{-}BuO^{\bullet} + KClO_4 \longrightarrow Ph_3COBu\text{-}t$$

Triphenylchloromethane reacts in the same manner. The signal of the triphenylmethyl radical is well resolved and increases at the begining of the reaction, decreases to zero.

A solution of Ph_3CX in THF (0·1 mole/l) was mixed with excess of t-BuOK directly in the cavity of the ESR spectrometer (pure argon atmosphere). A graph of the variation of the intensity of the ESR signal of the triphenylmethyl radical with time is presented in Fig.1. The maximum of the curve corresponds to a concentration of $Ph_3C^{\bullet}$ radicals of $1{\cdot}5.10^{-3}$ mole/l. The same picture appears in the Ph_3CCl-PhONa system (dioxane-THF solution). If a mixture of pyridine and phenol is used instead of phenoxide the concentration of triphenylmethyl radicals corresponds about 0·1% of the total amount of triphenylchloromethane.

The use of potassium 2,4,6-tri-t-butylphenoxide in lieu of tert-butoxide yielded the stable tri-2,4,6-tert-butylphenoxy radical (100%). The intensity of the ESR signal of this radical with time is presented in Fig.2.

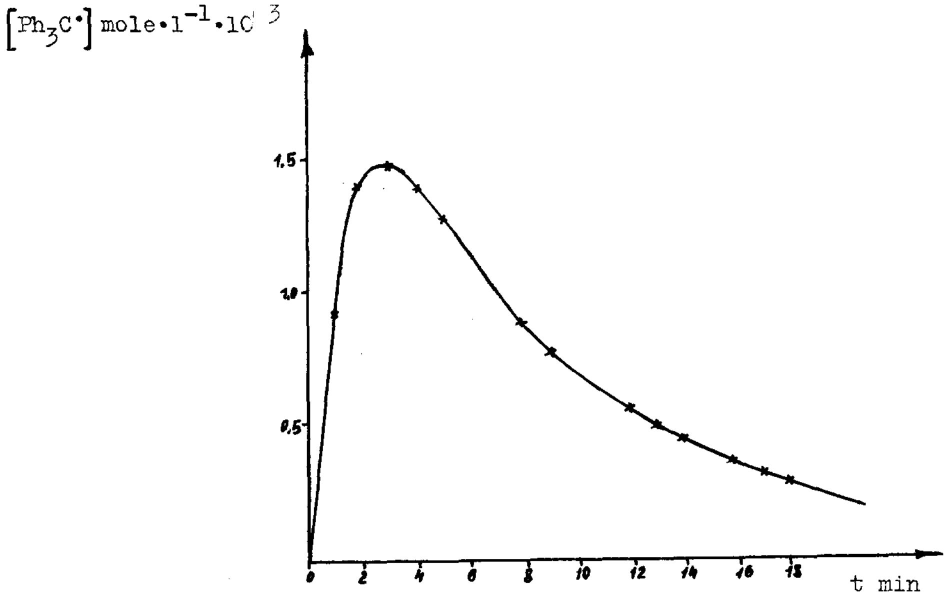

Fig. 1

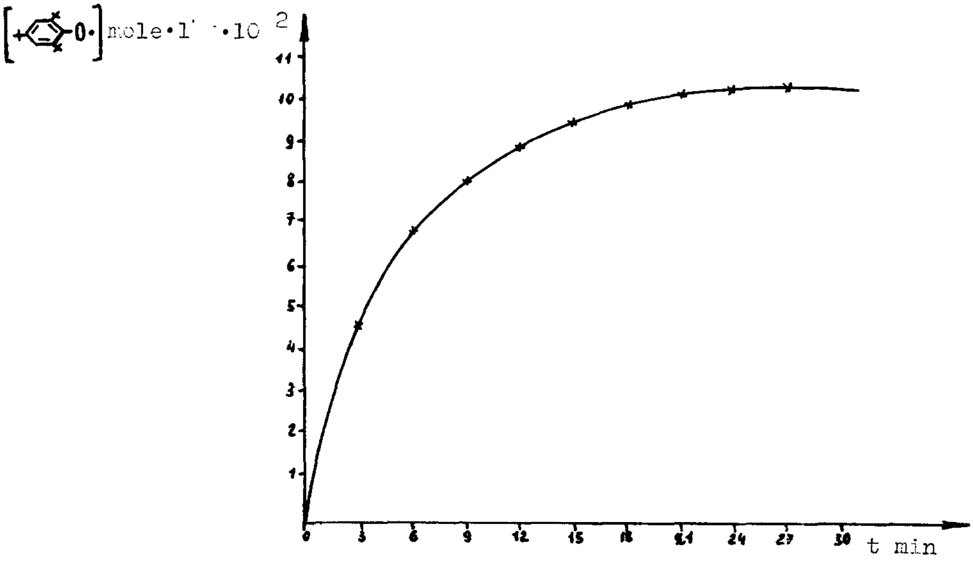

Fig. 2

The formation of an ether does not take place in this case and the triphenylmethyl radicals first formed gradually dimerise.

It follows that this classic heterolytic reaction of S_N1 type seems to be a two-step process and the first step of the overall process is an electron transfer reaction.

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