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FORMATION OF RADICAL CATIONS FROM 1,4-DIALKOXYBENZENES IN NITRO COMPOUNDS IN THE PRESENCE OF $AlCl_3$

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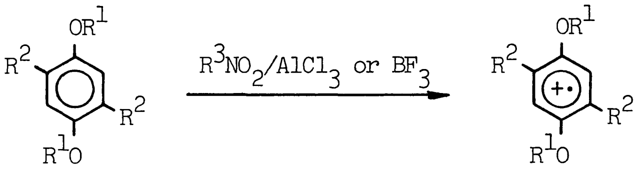
The electron transfer from 1,4-dialkoxybenzenes giving rise to the corresponding radical cations takes place not only in nitromethane but also in other nitro compounds, aliphatic and aromatic one, in the presence of $AlCl_3$ or BF_3. The reaction is reversible and affected by substitution and concentration of the 1,4-dialkoxybenzenes and nature of the nitro compounds. $(RNO_2)_2AlCl_2^+$ may be suggested to be the electron acceptor in the system.

The fact that 1,4-dimethoxybenzene (DMB) undergoes one electron transfer quantitatively to give DMB radical cation in CH_3NO_2 containing anhydrous $AlCl_3$[1] has drawn our attention to investigate the nature of this reaction because little is known about chemistry of the reaction which has been utilized as a generation method of radical cations for ESR studies.[1,2]

We now have found that the reaction takes place not only in CH_3NO_2 but also in other nitro compounds, aliphatic and aromatic one, in the presence of $AlCl_3$ and that the reaction is reversible and is affected by substitution and concentration of the 1,4-dialkoxybenzenes and nature of the nitro compounds.

It was confirmed by identification of paramagnetic species with ESR technique that the reactions proceed as the following scheme.



(I) (II)

Observed hyperfine splitting constants of radical cations (II) in a typical case are given in Table 1.

Table 1. Hyperfine splitting constants of (II; R^1=Me) in CH_3NO_2-$AlCl_3$ at room temperature

R^2	H[a]	Me[b]	n-Pr	i-Pr	t-Bu
$a_H(OCH_3)$	3.36	3.19	2.93	2.92	2.95
$a_H(R^2)$		4.29	2.30	2.92	
a_H(ring)	2.26	0.59	0.63	0.53	0.90

a Ref.2 b Ref.3

The electron transfer in the aliphatic nitro compounds is extremely fast, e.g. upon addition of (I; R^1=Me, R^2=n-Pr) (0.1 mg) into the aliphatic nitro compounds (1 ml) containing anhydrous $AlCl_3$ (2 mg) at room temperature, the reaction was completed instantaneously to give (II; R^1=Me, R^2=n-Pr) quantitatively in all aliphatic cases (R^3=Me, Et, i-Pr, cyclohexyl, t-Bu, 1-adamantyl, benzyl, and phenetyl) whereas in nitrobenzene the reaction was completed up to 77% within 10 min. $AlCl_3$ could be replaced with BF_3, but it decreases the reactivity. The radical concentrations were estimated by overmodulating the ESR signals and comparing the signal intensities under similar conditions with that of DPPH as standard. The results indicate that the electron transfer is not affected by structural change in aliphatic nitro compounds but decreases in the reactivity in aromatic one. Thus, influence of substituents R^1 and R^2 of (I) on the reactivity is examined in nitrobenzene (Table 2).

Table 2. Influence of substituents of (I) on the electron transfer in nitrobenzene containing $AlCl_3$ at room temperature[a]

R^1	Me	Me	Me	Me	Me	Me	Et	Et
R^2	H	Me	n-Pr	i-Pr	t-Bu	Cl	H	i-Pr
Radical concn. (%)[b]	4	70	77	70	30	1	8	81

a (I) (1×10^{-2}m mole) was dissolved in nitrobenzene (1 ml) containing $AlCl_3$ (0.15 g).

b The concentrations were determined 5 min. after mixing all reagents. DPPH in nitrobenzene was refered as a standard.

As seen in Table 2 the effect of R^2 on the reactivity is much remarkable compared to that of R^1 where the Et group promotes the reaction slightly more than the Me group, indicating that electron releasing alkyl groups promote the reaction. Decrease in the reactivity for t-butyl compound is due to the competition between the electron transfer and the de-t-butylation.[4]

Radical cation (II; R^1=Me, R^2=n-Pr) is considerably stable in the aromatic nitro compounds. Influence of substituents of aromatic nitro compounds on the electron transfer was examined (Figure 1). Although electron withdrawing groups decrease the reactivity, it seems to be difficult to interpret satisfactorily the results because electron releasing groups also slightly decrease the reactivity.

Formation of radical cations (II) is also affected by the concentration of (I) in nitro compounds. The high concentration of (I) decreases the absolute concentration of (II), which is increased by further dilution with the nitro compounds. These facts indicate that there is such an equilibrium electron transfer as seen in the reaction of N,N,N',N'-tetramethyl-p-phenylenediamine with tetrachloro-p-benzoquinone,[5] and it would be expected to produce corresponding nitro compound radical anions such as $R^3NO_2^{-\bullet}$ along with (II). However, no radical anion was detected but only the radical cation (II) in the ESR spectrum of the every reaction mixture, so some other diamagnetic reducing species instead of $R^3NO_2^{-\bullet}$ must be considered to form in the system. This reversibility of the reaction can be also shown by the fact that addition of H_2O to the solution of (II) (∿100%) in R^3NO_2-$AlCl_3$ resulted in the recovery of (I) and R^3NO_2 in nearly quantitative yield, respectively, where H_2O acts giving rise to the reverse electron transfer from the reducing anion to the radical cation (II) since H_2O itself does not behave as reducing agent for aromatic radical cations.[7∿12]

Taking into account the ionization equilibrium in the system of CH_3NO_2-$AlCl_3$,[6] it is

$$CH_3NO_2 + AlCl_3 \longrightarrow CH_3NO_2\cdot AlCl_3$$

$$2CH_3NO_2\cdot AlCl_3 \rightleftharpoons (CH_3NO_2)_2AlCl_2^+ + AlCl_4^-$$

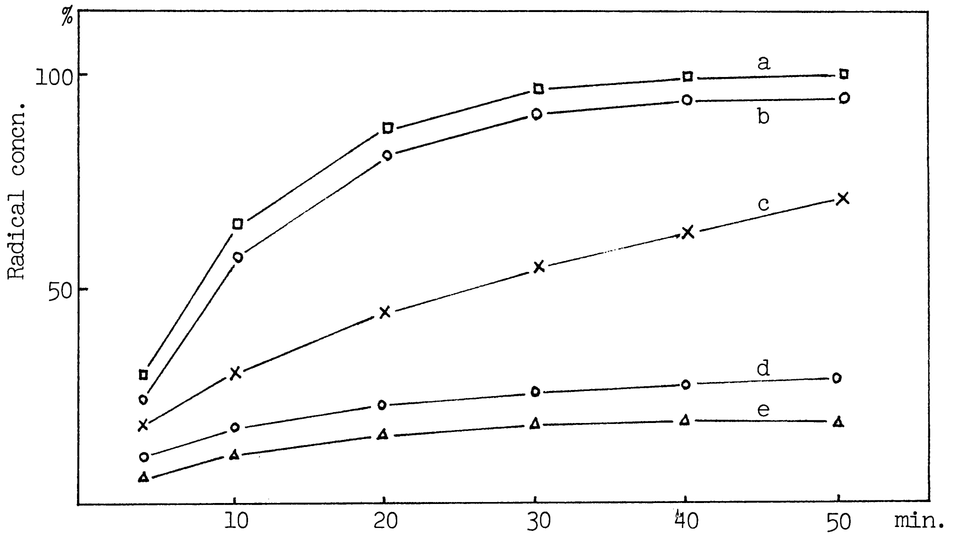
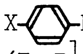


Figure 1. Time course of the reaction of (I; R^1=Me, R^2=*n*-Pr) to (II; R^1=Me, R^2=*n*-Pr) in X--NO_2 showing increase of the radical cation concentrations with time. (I; R^1=Me, R^2=*n*-Pr) (5×10^{-4}m mole) was dissolved in a solution of the *p*-substituted nitro compound (1×10^{-3}m mole) and $AlCl_3$·(10 mg) in dry benzene (1 ml). a; X=H, b; X=OMe, c; X=CH_3, d; X=Cl, e; X=$COCH_3$.

expected that the cationic species $(R^3NO_2)_2AlCl_2{}^+$ could function as the electron acceptor in the electron transfer to give the diamagnetic reducing species, e.g. $(R^3NO_2)_2AlCl_2{}^-$ or some others.

This case suggests that carbonium ions also can function as acceptors for the electron transfer from (I). In fact, (I; R^1=Me, R^2=*i*-Pr) in which the aromatic substitution will not easily take place because of steric hindrance gave significant amounts of (II; R^1=Me, R^2=*i*-Pr) in $C_6H_5CH_2Cl$ or C_6H_5COCl in the presence of $AlCl_3$.

Recently, NO^+ produced by heterolysis of CH_3NO_2 has been suggested to be the oxidizing species in the CH_3NO_2-$AlCl_3$ system in an electrochemical study on the system.[13] However, the possibility of NO^+ being the reactive species in our case can be ruled out because the formation of NO^+ is slow[13] whereas the electron transfer giving (II) from (I) is extremely fast and because of the reversibility of the reaction. Furthermore, such heterolysis for giving NO^+ does not easily occur in the aromatic nitro compounds. The formation of NO^+ must be considered to associate with the instability of (II) in the system, which was found to depend upon the instability of the aliphatic nitro compounds against $AlCl_3$, increasing in order of primary < secondary < tertiary. Thus, the radical cations (II) in the aliphatic nitro compound solutions decompose on standing at room temperature to give a complex mixture of products, some of them have been identified.

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