PHYSICAL CHEMISTRY

A. A. Medzhidov, A. L. Buchachenko, M. B. Neiman

1965

SovietRxiv

Abstract

Full Text

PHYSICAL CHEMISTRY

A. A. Medzhidov, A. L. Buchachenko, M. B. Neiman

ON THE POSSIBILITY OF ACID-BASE CATALYSIS OF RADICAL REACTIONS

(Presented by Academician V. N. Kondrat' ev on 22 IX 1964)

Liquid-phase reactions of radicals with saturated molecules, proceeding, for example, with abstraction of a hydrogen atom, usually require considerable activation energies. Such reactions are comparatively slow. However, there apparently exist fundamental possibilities for accelerating such radical reactions, for converting them into a catalytic regime. The present work illustrates such a possibility using the example of the reaction of nitroxide radicals with amines and diamines.

Table 1

Values of kK_R for certain nitroxide radicals

No.	Radical	kK_R, $l^2/mol^2 \cdot sec$
I	structural formula: 2,2,6,6-tetramethyl- -piperidone nitroxide radical, with $O = C$, $N - O\cdot$, and four CH_3 groups	$2.1 \cdot 10^3$
II	structural formula: corresponding hydroxypiperidine nitroxide radical, with H, HO, $N - O\cdot$, and four CH_3 groups	$3.8 \cdot 10^3$
III	structural formula: CH_3O-substituted diphenyl nitroxide radical, $CH_3O - C_6H_4 - N(O) - C_6H_4 - OCH_3$	$26.7 \cdot 10^3$

The stable nitroxide radicals we used (see Table 1) are stable in acetic acid; their interaction with N,N -dialkyl-*p*-phenylenediamines and N-alkyl-N-aryl-*p*-phenylenediamines in hydrocarbons, alcohols, and acetone likewise does not occur.

However, in mixtures of acetic acid with these solvents, rapid disappearance of the radicals is observed, the rate of which increases as the pH of the medium decreases. In this process, the intermediate radical products formed are the cation radicals of the corresponding amines ([1]).

To study the final reaction products, 1.32 g of N,N -di-*n*-octyl-*p*-phenylenediamine and 1.35 g of 2,2,6,6-tetramethyl- -piperidone nitroxide (radical I) were dissolved in a mixture of 50 ml of acetic acid and 50 ml of acetone; the mixture was left for several days at room temperature in the absence of oxygen. The solvents were then distilled off in vacuo. The dark residue was made alkaline with K_2CO_3 and extracted with water; the aqueous solution was saturated with NaCl, and its contents were extracted with small portions of ether. The ether extract was dried with calcined K_2CO_3, after which the ether was distilled off. This gave 1.15 g (theoretical amount 1.35 g) of an almost colorless crystalline substance with m.p. 90°. After recrystallization from hexane, m.p. 92°. Elemental analysis of the product corresponds to 2,2,6,6-tetramethyl- -piperidone hydroxylamine.

Found, %: C 63.17; H 10.13; N 8.15
Calculated, %: C 63.12; H 10.10; N 8.18

From the dark resinous product, a small amount (0.3 g) of the starting paraphenylenediamine was isolated. The remaining product is a resin. Thus, the initial stage of the transformations

can be represented in the following form:

$$\mathrm{R}\cdot + \mathrm{AH} \xrightarrow{\mathrm{H}^+} \mathrm{RH} + \mathrm{A}\cdot\mathrm{H}^+,$$

where R· and RH are a nitroxide radical and its hydroxylamine, and AH and $\mathrm{A}\cdot\mathrm{H}^+$ are the diamine and its cation-radical, respectively. Further, special experiments showed that the cation-radical $\mathrm{A}\cdot\mathrm{H}^+$ does not react with R·, and its disappearance occurs by disproportionation according to scheme ([2]):

$$2\mathrm{A}\dot{\mathrm{H}}^+ \rightleftarrows \mathrm{A} + \mathrm{AH} + 2\mathrm{H}^+,$$

where A is quinonediimine, which is highly unstable ([3]). The resinous residue formed in our case is apparently the product of its transformation.

Thus, the radical is converted into hydroxylamine, and the diamine is ultimately dehydrogenated into quinonediimine; that is, an acid-catalyzed radical reaction of abstraction of hydrogen atoms from the diamine by the radical takes place.

Typical semilogarithmic anamorphoses of kinetic curves for the disappearance of nitroxide radicals (concentrations are expressed in moles per liter)

Fig. 1. Typical semilogarithmic anamorphoses of kinetic curves for the disappearance of nitroxide radicals (concentrations are expressed in moles per liter)

To elucidate the mechanism of such catalysis, the kinetic laws governing the disappearance of radicals in the presence of N, N'-di-*n*-octyl-*p*-phenylenediamine in mixtures of acetone with acetic acid were studied in detail. The reaction was carried out under conditions such that the rate of formation of cation-radicals was small; here the concentration relation $[AH^+] \ll [R\cdot]$ is satisfied.

Subsequently, these conditions make it possible to take into account only the direct transfer reaction and to avoid complications due to side processes. The rate of radical disappearance was measured by the EPR method at various initial concentrations of the amine (with $[AH]_0 \gg [R]$) and at different pH values of the medium.

Figure 1 shows semilogarithmic anamorphoses of typical kinetic curves for the disappearance of radicals, from which it is seen that radical disappearance obeys well the first-order kinetic equation with an effective rate constant φ. Figure 2 shows the dependence of φ on the initial concentration of amine $[AH]_0$, and Fig. 3 the dependence between the logarithm of the reduced constant $\varphi/[AH]_0$ and the pH of the medium, the slope of the straight line in the latter case being equal to unity. The observed linear dependences of the rate of radical disappearance on the concentration of the radical, the diamine, and the concentration of protons mean that the rate of radical disappearance obeys the following kinetic equation:

$$-\frac{dR}{dt} = k_{\text{eff}}[R\cdot][AH]_0[H^+]. \tag{1}$$

Here k_{eff} is the effective rate constant, and $[H^+]$ is the concentration of protons (here and below, by H^+ is meant, of course, a solvated proton).

The most probable scheme satisfying the kinetic laws found is the following:

$$R\cdot + H^+ \rightleftarrows R\cdot H^+,$$

$$AH + H^+ \rightleftarrows AH_2^+,$$

$$R\cdot H^+ + AH \xrightarrow{k} RH + A^+H\cdot.$$

This scheme provides for the equilibrium formation of the protonated form of the radical $R\cdot H^+$ and of the amine AH_2^+, followed by electron transfer from the amine to the protonated radical. Cation radicals, as already indicated,

are consumed in disproportionation (2) and, under the conditions of kinetic experiments, are not formed in measurable concentrations.

Fig. 2 and Fig. 3

Fig. 2. Dependence of φ on the initial concentration of amine at 20°.
1—pH 5.5, 2—pH 4.95, 3—pH 4.60

Fig. 3. Dependence of the logarithm $\varphi/[\mathrm{AH}]_0$ on the pH of the medium at 20°

Analyzing the scheme presented, one can obtain the following expression for the rate of disappearance of radicals (at small degrees of their protonation):

$$-\frac{dR}{dt} = \frac{kK_{\mathrm{R}}[\mathrm{H}^+]}{1 + K_{\mathrm{A}}[\mathrm{H}^+]}[\mathrm{R}\cdot][\mathrm{AH}]_0. \tag{2}$$

For $K_{\mathrm{A}}[\mathrm{H}^+] \gg 1$

$$-\frac{dR}{dt} = \frac{kK_{\mathrm{R}}}{K_{\mathrm{A}}}[\mathrm{R}\cdot][\mathrm{AH}]_0, \tag{3}$$

for $K_{\mathrm{A}}[\mathrm{H}^+] \ll 1$

$$-\frac{dR}{dt} = kK_{\mathrm{R}}[\mathrm{R}\cdot][\mathrm{AH}]_0[\mathrm{H}^+] \tag{4}$$

with the effective rate constant in equation (1)

$$k_{\mathrm{eff}} = kK_{\mathrm{R}}.$$

In our case, apparently, the latter condition is realized, and equation (4) agrees well with the experimentally obtained equation (1). Table 1 gives the values of kK_{R} for several radicals.

The pK values of azoxy radicals are unknown (unlike those of phenoxyl radicals [4,5]); this does not permit determination of the absolute values of k.

It should be noted that in the scheme considered the following reactions were not taken into account:

$$\text{a) } \mathrm{R}\cdot + \mathrm{AH} \rightarrow \mathrm{RH} + \mathrm{A}\cdot,$$

$$\text{b) } \mathrm{R}\cdot + \mathrm{AH}_2^+ \rightarrow \mathrm{RH} + \mathrm{AH}^{\cdot +},$$

$$\text{c) } \mathrm{R}\cdot + \mathrm{AH}_2^+ \rightarrow \mathrm{R}^- + \mathrm{AH}_2^{2+}.$$

The first of these reactions, as was noted at the beginning, proceeds immeasurably slowly. The rate of the second reaction should be still smaller, than the first, since the positive charge increases the energy of homolytic bond cleavage:

Bond	$H_2O^+ - H$	$HO - H$	$H - O^-$	NH_4^+	NH_3
Bond energy, kcal/mol	158	117	98	130	105

Reaction c) is also unlikely, since removal of a second electron from the cation AH_2^+ is apparently energetically hindered.

Thus, electron transfer from an amine molecule to a radical proceeds with the participation of the protonated form of the radical. The stationary concentration of this form is low and is not detected by the EPR method.

However, the presence of the protonated form of the radical is not an obligatory condition for electron transfer. In a number of cases transfer may also occur to the free radical[6], the possibility of this being determined by the oxidation-reduction potentials of the interacting pairs.

Thus, in general form, for the case of the interaction of nitroxyl radicals with disubstituted *p*-phenylenediamines one may write:

$$2\,\text{Diamine} + 2\,\text{R}\cdot \xrightarrow{+2\text{H}^+} 2\,\text{RH} + 2\,\text{Cation Radical}$$

$$2\,\text{Cation Radical} \xrightarrow{-2\text{H}^+} \text{Quinonediimine} + \text{Diamine}$$

or, omitting the intermediate catalytic stages,

$$\text{Diamine} + 2\text{R}\cdot \rightarrow \text{Quinonediimine} + 2\text{RH}.$$

Thus, the fundamental possibility of acid-base catalysis of radical reactions has been shown here; its meaning consists in the fact that nuclear motions in the activated complex of the uncatalyzed reaction are replaced by electronic motions in the limiting stage of the catalyzed reaction.

Institute of Chemical Physics
Academy of Sciences of the USSR

Received
5 VIII 1964

REFERENCES

1. M. B. Neiman, A. A. Medzhidov et al., DAN, **154**, 387 (1964).

2. J. E. Lu Valle, D. B. Glass, A. Weissberger, J. Am. Chem. Soc., **70**, 2223 (1948).

3. L. Michaelis, M. P. Schubert, S. Granick, J. Am. Chem. Soc., **61**, 1981 (1939).

4. E. Land, G. Porter, E. Strachan, Trans. Farad. Soc., **57**, 1885 (1961).

5. E. Land, G. Porter, Trans. Farad. Soc., **59**, 2027 (1963).

6. V. Franzen, Ber., **88**, 4697 (1955).

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