Tetrahedron Letters No.18, pp. 1333-1336, 1971. Pergamon Press. Printed in Great Britain.

BRÖNSTED TYPE CORRELATION FOR TERT. BUTYL HALIDE SOLVOLYSIS UNDER THE ACTION OF METAL IONS

E.S.Rudakov, I.V.Kozhevnikov
Institute of Catalysis, USSR Academy of Sciences,
Siberian Division, Novosibirsk, USSR

(Received in UK 12 March 1971; accepted for publication 25 March 1971)

C-X bond heterolysis (mechanism S_N1) due to the reaction $RX + M^+ \xrightarrow{k_1} R^+ + MX$ is accelerated by metal ions M^+ (Lewis acids) which form stable halide complexes MX with reagent X^- (1-3). The rate law found was $d[RX]/dt = k_0[RX] + k_1[M^+][RX]$ where k_0 is the rate constant of the RX solvolysis in the same solvent. Tert. butyl halides proved to be suitable substrates for extensive research of the rate-equilibrium correlations for such reactions.

We have found that the values of k_1, k_0, and stability constants of the complex $K = [MX]/[M^+][X^-]$ are connected by the Brönsted type equation

$$\lg(k_1/k_0) = -0.7 + 0.84 \lg K \qquad (I)$$

which covers all variations of metal, RX halide (where $R = (CH_3)_3C-$, X = F, Cl, Br), and solvent. The data for the following reaction sets are shown in the Figure.

1. Hydrolysis of t-BuF in water, 25° (3). Ions: Zr(IV), Th(IV), Sc(III), Al(III), Fe(III), Be(II), Ga(III), H(I), Mg(II), Zn(II), Cd(II). The reactions with Be(II), Mg(II), Zn(II), and Cd(II) were studied by a gas-chromatographic method. The value of $k_0 = 3.2 \cdot 10^{-7}$ sec^{-1} found by the conductivity method is in agreement with the data (4). A aquochromium(III) ion was found to be inactive for the C-F bond heterolysis in water in spite of the high stability of the CrF^{2+} complex (lgK = 5.20 (5)). This result is in accord with the extremely slow rate of water exchange between

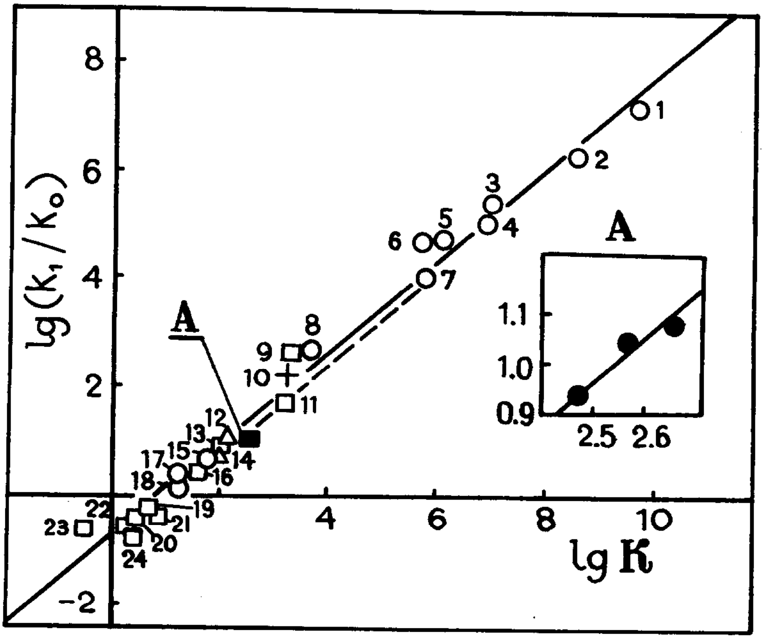

Fig. - Plot of lg(k_1/k_0) vs. lgK for the tert. butyl halide solvolysis under the action of metal ions (Lewis acids). k_1/k_0 and K in M^{-1}.

○ - t-BuF in water, 25° (3); ions: 1-Zr(IV), 2-Th(IV), 3-Sc(III), 4-Al(III), 5-Fe(III), 6-Be(II), 7-Ga(III), 8-H(I), 15-Mg(II), 17-Zn(II), 18-Cd(II).

□ - t-BuCl in 32 wt% EtOH - H_2O, 25° (2); ions: 9-Ag(I), 11-Bi(III), 13-Cd(II), 16-Pb(II), 19-Tl(I), 20-Co(II), 21-Mn(II), 22-Cu(II), 23-Ga(III), 24-Zn(II).

△ - t-BuBr in 44.6 wt% EtOH - H_2O, 20°; ions: 12-Cd(II), 14-Pb(II).

+ - t-BuCl in nitromethane, 75° (8); catalyst: 10-HCl.

● - t-BuCl, 25°, ion Cd(II) (7); 30, 35, and 40 wt% EtOH - H_2O; these data are shown scaled up in A.

— — — Decomposition of nitramide catalyzed by bases (9, 10).

aquochromium(III) ion and sovent H_2O.

2. Solvolysis of t-BuCl in 32 wt% EtOH - H_2O, 25° (2). Ions: Ag(I), Bi(III), Cd(II), Pb(II), Tl(I), Co(II), Mn(II), Cu(II), Ga(III), Zn(II). Activities of Tl(III), Hg(II), and Pd(II) ions were found to be too high to be measured by our methods.

3. Solvolysis of t-BuBr in 44.6 wt% EtOH - H_2O, 20°. Ions: Cd(II), Pb(II). These results were obtained as those described in (3).

All the metal ions were added in the form of nitrates. The K values in the sets 1-3 for water solutions were used (5). The change of lgK with the addition of 30 and 44 wt% of EtOH accounts for about 0.3 and 0.5 unit according to the data (6), which is close to the experimental inaccuracies in determination of k_1,k_0 and K

4. Solvolysis of t-BuCl, 25°, ion Cd(II) (7). Variation of the medium: 30, 35, and 40 wt% EtOH - H_2O. The values of K in these media have been taken from (6). These data are shown scaled up in A. The slope of the line is the same, $\beta = 0.84$, but the line is displaced by 0.3 unit to the right.

5. Isotopic ^{36}Cl exchange between t-BuCl and $H^{36}Cl$ in nitromethane at 75°. Catalyst: HCl (undissociated molecules). In accordance with previous data (8), for this reaction $10^6k\ (sec^{-1}) = 2.4 + 340[HCl]$, hence $k_1/k_0 = 142\ M^{-1}$. The value of $K = 1700\ M^{-1}$ the HCl_2^- complex has been estimated from the data of Table 3b of the same work.

We would like to draw attention to the general character of the correlation (Fig.). The equation (I) is obeyed for the ions differing in charge, electron structure, solvation energy including the H_3O^+ ion which accelerates the C-F bond heterolysis in accordance with the K value of the HF complex. The uncharged electrophiles (HCl in nitromethane) act in a similar way. The generality is also demonstrated with X variable, since different X's(e.g. X = F and Cl) conform with different sets of active metals, and solvent variation (H_2O, H_2O - EtOH, CH_3NO_2).

The relation found is like the Brönsted equation for general acid-base catalysis. As far as the form is concerned equation (I) seems to be however a more suitable one, with the relative rate k_1/k_0 being used. In this case the intercept does not depend on the substrate and solvent. It should be noted that equation (I) is also well obeyed for the Brönsted and Pedersen data (9, 10) for the decomposition of nitramide catalyzed by bases (anions of carboxylic acids and ring-substituted anilines).

REFERENCES

1. E.S.Rudakov, I.V.Kozhevnikov, Dokl. Akad. Nauk SSSR, 186, 354 (1969).
2. E.S.Rudakov, I.V.Kozhevnikov, Organic Reactivity (Tartu), 6, 560 (1969).
3. E.S.Rudakov, I.V.Kozhevnikov, Organic Reactivity (Tartu), 6, 573 (1969).
4. R.E.Robertson, R.L.Heppolette and J.M.W.Scott, Can. J. Chem., 37, 803 (1959).
5. Stability Constants of Metal Ion Complexes. Special Publication No. 17. London. Chemical Society. 1964.
6. Ya.I.Tur'yan, B.P.Zhantalai, Zhur. Neorg. Khim., 5, 1748 (1960).
7. V.P.Tretyakov, E.S.Rudakov, V.B.Bistrenko, Organic Reactivity (Tartu), 6, 542 (1969).
8. Y.Pocker, J. Chem. Soc., 1960, 1972.
9. J.N.Brönsted, K.Pedersen, Z. Phys. Chem., 108, 185 (1924).
10. S.W.Benson, "The Foundation of Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, 1960, p. 567.