of substantial quantities of certain key intermediates and to Mr. Sergey V. Chodsky for technical assistance.

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THE SALT EFFECT IN THE AROMATIC NUCLEOPHILIC SUBSTITUTION REACTION[1]

Sir:

The effect of added neutral salts upon the velocity of the second order of the ion–dipole aromatic nucleophilic substitution reactions of lithium, sodium and potassium methoxides with 2,4-dinitrochlorobenzene has been investigated at 25°. The rates were studied in absolute methanol solvent as a function of reactant ($LiOCH_3$, $NaOCH_3$, and $KOCH_3$) in the presence of added cations (Li^+, Na^+, and K^+) and added anions ($C_2H_3O_2^-$, I^-, Br^-, ClO_4^-, Cl^-, and NO_3^-). The reaction of $NaOCH_3$ in the presence of added $LiClO_4 \cdot 3H_2O$ also was studied in a 50 volume % methanol-benzene solvent.

For reactions without added salts, the rate constants (1 mole^{-1} sec.$^{-1}$) were: $LiOCH_3$, 0.0242; $NaOCH_3$, 0.0262; $KOCH_3$, 0.0278. A consistent pattern of salt effects is typified by the data for the $LiOCH_3$ reaction shown in Fig. 1. At low concentrations of added salt, each cation exhibits an individual effect, added to that of the cation introduced along with the reactant methoxide. The anions cause an additional secondary effect. The reaction rate increases for acetate > Cl^-, Br^- > I^-, NO_3^- > ClO_4^-. Salt effects are more pronounced in solvents of lower dielectric constant. The observed effects cannot be correlated with changes in ionic strength of the reaction medium as found by Bolto and Miller.[2]

A qualitative explanation of the effect of lithium salts assumes the equilibrium

$$LiOCH_3 \rightleftarrows Li^+ + {}^-OCH_3$$

The addition of a salt providing Li^+ as a common ion should shift this equilibrium to decrease the concentration of the reactant, OCH_3^-. Since the effective concentration of added Li^+ will depend on the degree to which it remains associated with the added anion, the rate will differ with different added salts. This assumes that the ion pair reacts at a negligible rate compared to that for the ion. A similar interpretation has been used to account for the variation in rate of decarboxylation of trichloroacetic acid.[3] The observed effect of anions on reaction rate thus can be interpreted to suggest that the order of attraction for lithium ions in methanol is Ac^- > Cl^-, Br^- > NO_3^-, I^- > ClO_4^-.

The fact that $NaOCH_3$ and $KOCH_3$ react faster suggests that the corresponding equilibria involving these methoxides is shifted more to the right, providing a greater effective concentration of OCH_3^-. Conductivity data[4] suggest that more ion association occurs for $LiOCH_3$ than for $KOCH_3$ or $NaOCH_3$ in methanol. Potassium salts are strong electrolytes in methanol with dissociation constants of about 0.1 to 0.02.[5] It is known that potassium salts are stronger electrolytes than are lithium salts in acetone.[6] If a similar order of electrolyte strength holds for methanol solutions, then the effect of added potassium salts on the $LiOCH_3 \rightleftarrows Li^+ + {}^-OCH_3$ equilibrium would be to supply anions which would tend to associate more readily with Li^+ so that the equilibrium would be shifted to provide a greater concentration of OCH_3^-. This accounts for the increase in rate of the reaction. Sodium salts are not as effective as potassium salts, and the anion effects are consistent with those observed in the presence of Li^+ alone.

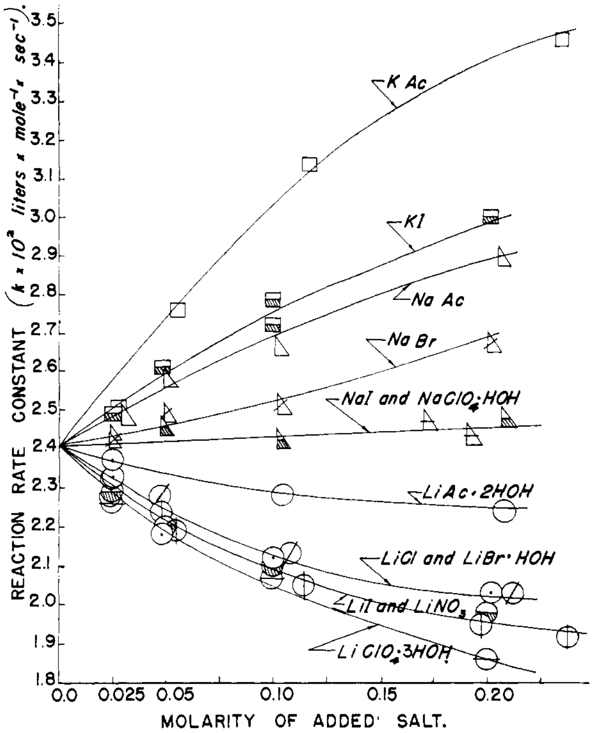

Fig. 1.—Lithium methoxide and 2,4-dinitrochlorobenzene.

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THE EFFECT OF NITRATE ION ON THE YIELD OF HYDROGEN FROM WATER RADIOLYSIS

Sir:

Solutions of calcium nitrate have been irradiated in the mixed fast neutron-γ-flux of the Harwell experimental reactor BEPO at a temperature of about 80°. Nitrate concentration was varied from 15.9 to 0.037 *M*. The thermal neutron dose was monitored using cobalt wire of high purity.[1] Energy deposition figures were derived using the data of

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[1] J. Wright, to be published.