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 $LiOCH_3 \rightleftharpoons Li^+ + {}^-OCH_3$ 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.

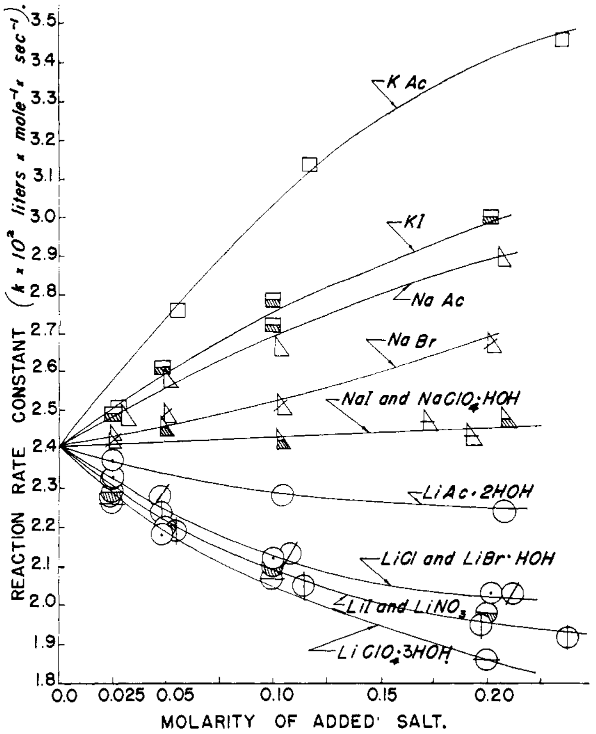

Fig. 1.—Lithium methoxide and 2,4-dinitrochlorobenzene.

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(1) This research supported by the Petroleum Research Fund of the American Chemical Society.

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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.

A. R. Anderson[2]; maximum energy deposition extended to 7 × 10^{22} e.v. per g. of solution. The main products were nitrite, oxygen and hydrogen: a low yield of nitrogen was observed from concentrated solution. The 100 e.v. yield of nitrogen (G_{N_2}) from a 9.4 M solution was (3.2 ± 0.6) × 10^{-3}.

Particular attention was paid to variation of hydrogen yield with $[NO_3^-]$. Calculation of G_{H_2} in the more concentrated solutions is complicated by absorption of energy by nitrate ion, but the complication is not serious for our purposes. For example, in the worst case (15.9 M solution), assuming that all fast neutron-γ energy deposited in solution is available for water decomposition, $G_{H_2} = 0.011 \pm 0.001$. Assuming that only the energy deposited directly in the water is available, $G_{H_2} = 0.025 \pm 0.003$. A value of 0.019 ± 0.009 embraces both these extremes. At concentrations below 1 M, difference between the two G values is less than experimental error. The figure shows a plot of G_{H_2} *vs.* $[NO_3^-]^{1/3}$. Linearity is evident up to $[NO_3^-]$ of about 1 M; the data over this region follow an equation of the type

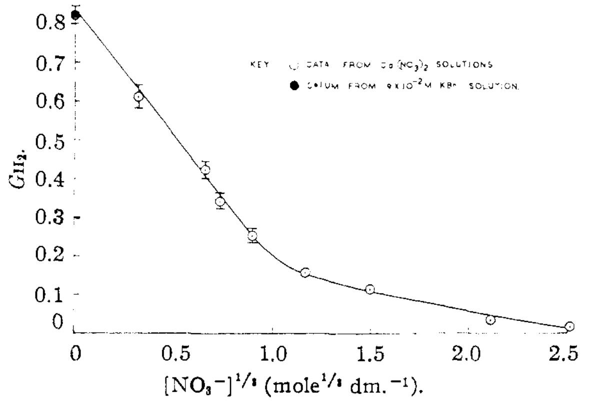

Fig. 1.—Variation of G_{H_2} with $[NO_3^-]^{1/3}$.

$$G_{H_2} = A - k[NO_3^-]^{1/3} \qquad (1)$$

Sworski[3,4] observed this relationship to hold for variation of $G_{H_2O_2}$ with $[Br^-]$ and $[Cl^-]$. Allen and Holroyd[5] confirmed and extended the Br^- data. The data of Schwarz[6] concerning the effect of $[Cu^{++}]$ and $[NO_2^-]$ on G_{H_2} can be expressed by equation (1). The table shows values of A and k for the various solute ions M; solutions are approximately neutral unless otherwise indicated.

M =	NO_3^-	Br^-	Br^- (pH 2)	Cl^- (pH 2)	NO_2^-	Cu^{++}
A =	0.84	0.68	0.78	0.75	0.44	0.44
k =	0.65	0.65	0.93	0.88	0.30	0.60

The significance of the "one-third power" relationship has been discussed qualitatively by Sworski.[3] The parameter k affords a measure of the probability that the ion in question will react with the appropriate radical (H or OH) as it diffuses out of a "hot spot." The similarity between values of k for various ions is noteworthy. Parameter A measures the hypothetical molecular yield at zero concentration. It is different for H_2 and H_2O_2, and for various types of ionizing radiation.[7] A was measured in the present case using a 1.9 × 10^{-2} M KBr solution, in which the radical back reaction is adequately suppressed.[8] The value of 0.82 ± 0.02 is in good agreement with the intercept at zero $[NO_3^-]$ in the figure.

The present results may be interpreted in terms of "capture" of H atoms by NO_3^-

$$NO_3^- + H \longrightarrow NO_2 + OH^- \qquad (2)$$

From the data it may be deduced that when the "average distance" between nitrate ions is 20 Å., about half of the H atoms available for H_2 production are consumed by reaction (1). Above a concentration of 1 M (when the "average distance" between ions is about 11 Å.), G_{H_2} decreases less rapidly as $[NO_3^-]$ is increased. In 15.9 M solution (melted crystals of $Ca(NO_3)_2 \cdot 4H_2O$) more than 97% of available H atoms are intercepted.

A complete account of the work, with due acknowledgments, will be published later.

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ATOMIC ENERGY RESEARCH ESTABLISHMENT
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A NEW POLYMERIC SULFUR-NITROGEN COMPOUND

Sir:

It has long been known that the reaction of sulfur chloride with ammonia gives sulfur nitride.[1-2] This substance, a cyclic tetramer, has the structure of an eight-membered ring composed of alternating sulfur and nitrogen atoms,[3] with four resonating double bonds. It may be reduced to the saturated analog, $H_4S_4N_4$.[4] It has been reported that the action of sulfur dichloride on ethylamine produces the corresponding N-ethyl derivative $(SNC_2H_5)_4$,[5] while other authors have found that n-butylamine and sulfur tetrachloride give $C_4H_9\text{-}N{=}S{=}N\text{-}C_4H_9$.[6] We have found that when methylamine is allowed to react with a hexane solution of sulfur dichloride, a low-molecular-weight plastic polymer having the approximate composition $(CH_3NS)_x$ is formed. Additional products are methylamine hydrochloride and an unidentified unstable yellow oil which is presumed to contain the cyclic tetramer. The polymer has been prepared in varying molecular weights, depending on how closely the relative amounts of the two reagents were controlled; *i.e.*, exact control leads to high molecular weights. In its lowest molecular weight form (*ca.* 600 as measured cryoscopically), the polymer

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