of methanolic sodium perchlorate. After removal by filtration of a small amount of purple powder, diamond-shaped blue platelets grew slowly from the deep blue filtrate.

The compound crystallizes in the monoclinic system, space group $C2/c$ or Cc, with four formulas in a unit cell of dimensions $a = 15.008$ (3), $b = 10.186$ (2), $c = 26.062$ (3) Å; $\beta = 100.48$ (1)°; $\rho_{\text{calcd}} = 1.654$, $\rho_{\text{obsd}} = 1.68(1)$ g/cm^3. The structure, shown in Figure 1, was solved by standard Patterson and Fourier methods using 1727 independent reflections ($2\theta \leq 45°$, $F_o > 4\sigma(F_o)$) collected on a Picker FACS-I-DOS diffractometer at 23 °C using monochromatized Mo Kα radiation. The value for the conventional discrepancy index, $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, at the present stage of refinement in $C2/c$ is 0.077. Further work, to test refinement in Cc and to choose the best model for refining a disordered perchlorate anion, is currently in progress and will be reported with full details of the structure determination at a later date.

As anticipated, the $Cu_2(im)^{3+}$ ion is incorporated into the circular cryptate macrocycle A using the two diethylenetriamine units at the poles of the cavity. Each copper(II) ion is further coordinated to a neutral imidazole (imH) ligand, achieving overall pentacoordination. As may be seen from the N-Cu-N bond angles (Figure 1), the copper geometry is best described as distorted trigonal bipyramidal, with N(1) and N(11) nearly on the axis and N(2), N(3), and N(21) defining the equatorial plane. The Cu-N bond lengths are similar to those in **2**^{3c} except for Cu-N(2) which is somewhat elongated. The two ether oxygen atoms of macrocycle A do not coordinate to the metal ions, the closest nonbonded Cu···O contact being an intermolecular one of 4.67 Å. A crystallographically required twofold axis passes through atom C(12) of the bridging imidazolate ligand. Further details of the geometry are given in the caption to Figure 1.

The synthesis and structure determination of $[Cu_2(imH)_2(im)\subset A](ClO_4)_3$ demonstrates the propensity of a cryptate macrocycle to incorporate a ligand bridged bimetallic center. An unbridged pair of copper(II) ions located inside the cavity of a macrotricyclic ligand has been structurally characterized recently.[11] The present compound is of relevance to the 4-Cu(II) form of bovine erythrocyte superoxide dismutase.[12] Additional physical and chemical studies of the complex will enable its evaluation as a model for the known or postulated functions of the protein.

Acknowledgments. This work was supported at Columbia University by NIH Research Grant No. GM-16449 from the National Institute of General Medical Sciences and by Grant No. CHE 76-18434 from the National Science Foundation.

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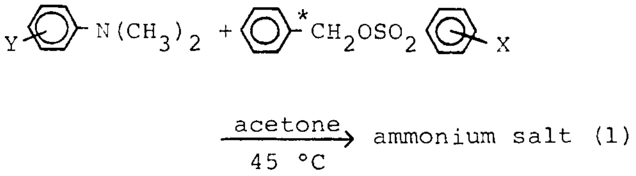
Received August 28, 1978

Carbon-14 Kinetic Isotope Effects in the Menschutkin-Type Reaction of Benzyl Benzenesulfonates with *N*,*N*-Dimethylanilines. Variation of the Effects with Substituents

Sir:

In 1975, we reported the first example of the bell-shaped behavior of carbon-14 isotope effects in the Menschutkin-type reaction of a series of benzyl benzenesulfonates with *N*,*N*-dimethyl-*p*-toluidine (eq 1, Y = *p*-CH_3).[1] The behavior indicated that the transition-state structure of the reaction varies with perturbation on the leaving group. The symmetry in terms of the force constants of two reacting bonds was demonstrated to be an important factor to determine the magnitude of the isotope effects as suggested by theoretical calculations.[2-6] Further study on the reaction has revealed that the magnitude of the effect varies not only with X but also with Y. In the present paper, the experimental results and an interpretation by means of the theory concerning the variations of transition state structures in S_N2 reactions are described.



The experimental procedure employed was the same as that reported in the previous paper.[1] The revised equation (eq 2) was used to calculate the isotope effects, where x is the fraction of reaction, A_x is the specific activity of the recovered product at x, and A_∞ is that at 100% reaction.[7] Isotope effects obtained are tabulated together with rate constants in Table I. The effects are plotted against substituent constants of X and Y in Figures 1a and 1b, respectively.[8]

$$A_x = A_\infty[1 - (1 - x)^{k^{14}/k^{12}}]/x \qquad (2)$$

The bell-shaped behavior is apparent in four cases out of six in Figure 1 including the one reported before (Figure 1a, Y = *p*-CH_3). Furthermore, it seems reasonable to regard the monotonous trends in Figure 1a in the cases of Y = H and *p*-CH_3O as parts of bell-shaped curves; for these two cases the maximum position presumably would be found at a more electron-withdrawing and a more electron-donating area of X, respectively. A shift of this type in the position of a maximum appears clearly in Figure 1b where the maximum for X = *m*-NO_2 occurs at a more electron-withdrawing area of Y compared with the maxima for X = H and *p*-Cl.

Since the magnitude of the kinetic isotope effects is connected directly with the transition-state structure, the variation of the isotope effect is expected to be explained as a result of variation of transition-state structures. According to Swain-

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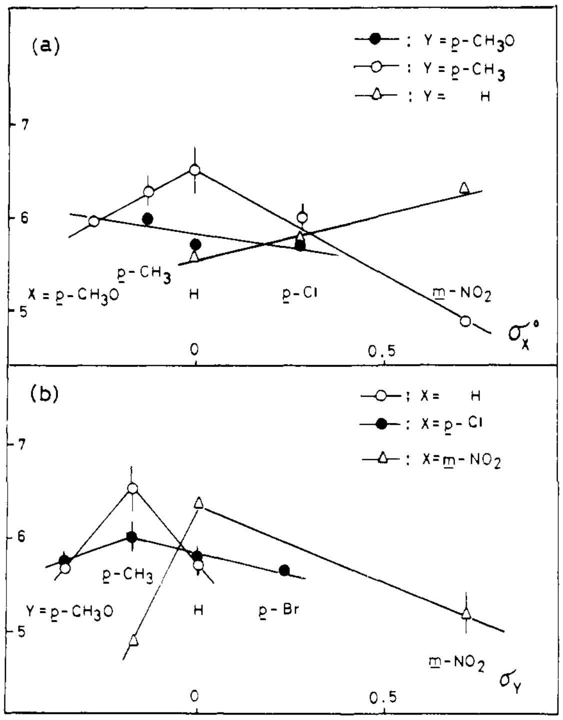

Figure 1. Variation of carbon-14 kinetic isotope effects in the Menschutkin-type reaction: (a) Y fixed, X varied; (b) X fixed, Y varied.

Table I. Rate Constants and Carbon-14 Kinetic Isotope Effects in the Menschutkin-Type Reaction of Benzyl Benzenesulfonates and *N,N*-Dimethylanilines[a]

Y	X	$10^4 k_2$, L mol^{-1} s^{-1}	k^{12}/k^{14}
p-CH$_3$O	p-CH$_3$	8.72 ± 0.21	1.148 ± 0.002
	H	17.1 ± 0.1	1.140 ± 0.003
	p-Cl	62.6 ± 0.8	1.142 ± 0.002
p-CH$_3$	p-CH$_3$O	2.36 ± 0.07	1.147 ± 0.002
	p-CH$_3$	3.84 ± 0.06	1.156 ± 0.005
	H	7.82 ± 0.01	1.162 ± 0.008
	p-Cl	27.2 ± 0.7	1.149 ± 0.004
	m-NO$_2$	252 ± 4	1.119 ± 0.003
H	H	3.41 ± 0.03	1.135 ± 0.003
	p-Cl	12.9 ± 0.1	1.143 ± 0.003
	m-NO$_2$	101 ± 1	1.158 ± 0.001
p-Br	p-Cl	3.88 ± 0.04	1.139 ± 0.002
m-NO$_2$	m-NO$_2$	8.60 ± 0.16	1.127 ± 0.006

[a] In acetone at 45 °C. Concentration: 0.007-0.015 L mol^{-1} in ester and 0.015-0.060 L mol^{-1} in nuclephile.

Thornton,[9] Thornton,[10] and Harris and Kurz,[11] a transition-state structure in an S$_N$2 reaction becomes more reactant-like (product-like) when the nucleophile becomes more (less) nucleophilic or the leaving group becomes a better (poorer) one. Judging from its maximum isotope effect (Figure 1b, X = H curve), the transition-state structure must be symmetric in terms of force constants of the two reacting bonds in the case of Y = p-CH$_3$ and X = H. Then, when the substituent Y is changed to a more electron-withdrawing one, H, the transition state shifts to be more product-like, and the unsymmetric transition state results in a smaller isotope effect. However, by then changing the substituent X to be more electron withdrawing (Figure 1b, changing from X = Y = H to X = m-NO$_2$, Y = H), the transition state recovers its symmetry and gives a larger isotope effect. Similarly, the monotonous trends in Figure 1a can be reasonably explained.

Another fact which is apparent from Figure 1 is that the maximum position shifts to a much smaller extent in Figure 1b than in 1a. In other words, substituent Y has a larger effect on the magnitude of the isotope effect than substituent X has. This may be a characteristic of a typical S$_N$2 reaction in which the bond formation is much more important than the bond breaking as a driving force of the reaction.

In conclusion, these kinetic isotope-effect results provide clear-cut evidence for the validity of the theory concerning the variation of the transition-state structure with substituent. Because of the advantageous characteristics of this reaction system, further investigations are underway.

Acknowledgment. We thank Professors Y. Yukawa and Y. Tsuno for helpful discussions. The present work was partly supported by a Grant-in-Aid (No. 07415, 347018, and 374163) for science research from the Ministry of Education.

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$$\log (A_\infty - A_x x) = k^{14}/k^{12} \log (1 - x) + \log A_\infty \qquad (3)$$

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Received August 3, 1978

Direct Tungsten-183 Nuclear Magnetic Resonance: a Powerful New Structural Tool for Heteropoly- and Isopolytungstate Chemistry

Sir:

Heteropoly and isopoly electrolytes constitute a distinct fundamental category of compounds of very sizable potential variety and importance.[1-3] However, only a relatively modest number of structural types has been elucidated.[2,3] Generally speaking, the poly*tungstates* are among the most diverse, stable, and readily purified of these compounds. This paper reports the first successful direct observation of ^{183}W NMR spectra for heteropoly- and isopolytungstates and, using several compounds, demonstrates that such spectra can be readily obtained (e.g., using a Bruker WH-90 FT spectrometer), are clear-cut, and provide a very powerful new tool for elucidation of structures in solution, with respect both to bonding and to relative atomic positions.

^{183}W, with spin ½ and at 14.27% abundance, is the only NMR-active isotope in natural W. Its sensitivity is 7.0×10^{-5} that of the proton. It was recently observed directly in simple WO_4^{-2} ion, WF$_6$, and WCl$_6$ by Banck and Schwenk,[4] who relied on the quadriga transform technique, which yielded broader lines than those reported herein. ^{183}W, again in simple compounds, has also been directly observed by Gansow,[5] who used a 180-MHz FT instrument. Various ^{19}F and ^{183}W NMR measurements on WF$_6$ have shown the W-F coupling constant to be small, the reported values[4-6] ranging from 41 to 48 Hz.