

lies much closer to the straight line than indicated in Fig. 2. Since the unsubstituted, the 5-substituted, the 5,6-dimethyl- and the 3,4,7,8-tetramethyl phenanthroline complexes all lie on the straight lines, there appears to be no specific steric effect present in the reactions of the 1,10-phenanthroline complexes of iron(III) with ferrous ions. It thus seems reasonable to suppose that the electron-transfer between the iron(III) complex and the ferrous ion does not take place in an activated complex in which the ferrous ion is located on the periph-

ery of a phenanthroline group, but instead it may be necessary for the ferrous ion to penetrate the space between the phenanthroline groups. This conclusion is supported by the fact that the entropy of activation of the reaction between ferrous ions and the tris-(1,10-phenanthroline)-iron(III) ion is considerably more negative than that of other iron(II)-iron(III) reactions.<sup>2</sup>

**Acknowledgment.**—We wish to thank Dr. R. W. Dodson for his interest in this work and for helpful discussions.

[CONTRIBUTION FROM THE DIVISION OF PURE CHEMISTRY, NATIONAL RESEARCH COUNCIL OF CANADA, OTTAWA, CANADA]

## The Temperature Dependence of the Solvent Isotope Effect<sup>1</sup>

BY R. L. HEPPOLETTE<sup>2</sup> AND R. E. ROBERTSON

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Rate data for the hydrolysis of isopropyl bromide in deuterium oxide have been determined over a temperature of 35 to 80°. By comparison with earlier data for hydrolysis in water, it was shown that the solvent isotope effect ( $k_{D_2O}/k_{H_2O}$ ) decreased with increasing temperature more rapidly than the solvent isotope effect for relaxation processes in bulk solvent. While this conclusion may be general for the hydrolysis of halides, it will not hold for the sulfonates where very much smaller values of  $d(k_{D_2O}/k_{H_2O})/dT$  are found. The sources of the solvent isotope effect for hydrolysis are examined. The results are shown to be consistent with the hypothesis that the major contribution to the observed characteristic differences resides in the relative structural stability of the initial state solvation shells.

In a recent paper<sup>3</sup> evidence was given to show how the "solvent isotope effect" obtained from the ratio of the rates of hydrolysis in light and heavy water ( $k_{D_2O}/k_{H_2O}$ ) might appreciably alter with temperature over the available experimental range. This conclusion was at variance with our earlier claim<sup>4</sup> that the temperature dependence of this ratio was small or zero and that of Swain and Bader<sup>5</sup> who concluded that the change in the solvent isotope effect with temperature was rapid at lower temperatures (say below 18°) but became small or zero above this temperature. Our earlier inference was based on limited data for the hydrolysis of the benzenesulfonates and methanesulfonates and is still essentially correct for those molecules which interact only weakly with water in the initial state. However, some doubts were raised as to the generality of this conclusion when the similarity was noted between the trend in the values of the  $k_{D_2O}/k_{H_2O}$  ratio for a series of halides reacting over a wide range of temperature and the corresponding variation in the values for the relative fluidity<sup>6</sup> ( $\phi_{D_2O}/\phi_{H_2O}$ ) and time of dielectric relaxation<sup>7</sup> ( $\tau_{D_2O}/\tau_{H_2O}$ ) for bulk H<sub>2</sub>O and D<sub>2</sub>O over the same range. But, while it may be quite reasonable to relate the temperature dependence observed in the ratios  $\phi_{D_2O}/\phi_{H_2O}$  and  $\tau_{D_2O}/\tau_{H_2O}$  to corresponding relative changes in structural stability of the bulk solvent (see below), a similar postulate for the temperature dependence of  $k_{D_2O}/$

$k_{H_2O}$  from data for a series of halides was less obvious. Thus, because of the possibility of specific differences in both the initial<sup>8</sup> and transition states,<sup>9</sup> our conclusions concerning the temperature dependence of  $k_{D_2O}/k_{H_2O}$  was less convincing in our recent paper<sup>3</sup> than if it had been based on data for a single compound obtained over a range of temperature. This has now been done and we report here the results of such a study for the hydrolysis of isopropyl bromide.

Isopropyl bromide was chosen as a suitable test compound, not only because other evidence suggested that in hydrolysis nucleophilic interaction was reduced compared to the primary halides but also because of convenient rates of hydrolysis in the accessible temperature range. Rate data for the hydrolysis of isopropyl bromide in H<sub>2</sub>O over the necessary range of temperature were already known<sup>10</sup> and could be expressed within experimental error by the equation ( $T$  in °K.)

$$\log k = -9306.912/T - 27.37569 \log T + 93.53701 \quad (1)$$

Corresponding data for hydrolysis in heavy water were obtained by the same conductometric techniques which have been described previously.<sup>11-13</sup> Temperature control and measurement as well as methods of calculation were uniform with the earlier work.

The isopropyl bromide used was a fractionated sample of Eastman White Label (b.p. 59-60° and  $n_{D_2O}^{20}$  1.4251) and was kept in the dark under refrigeration during the course of the investigation.

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(2) National Research Council of Canada Postdoctoral Fellow.

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(6) R. C. Harday and R. L. Cottingham, *J. Research Natl. Bur. Standards*, **42**, 573 (1949).

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D<sub>2</sub>O (99.8%) was obtained from Atomic Energy of Canada, a single stock solution containing 0.002 *M*. KBr backing electrolyte being used throughout the course of the study.

In Table I, rate data for the hydrolysis of isopropyl bromide in D<sub>2</sub>O for a range of temperatures

TABLE I  
RATE DATA FOR THE HYDROLYSIS OF ISOPROPYL BROMIDE IN DEUTERIUM OXIDE

Temp., °C.	$k_1$ , sec. <sup>-1</sup> × 10 <sup>5</sup>	<i>n</i> <sup>a</sup>	$k_{D_2O}/k_{H_2O}$
80.005	212.9 ± 0.2	4	0.789
74.829	129.6 ± .2	3	.788
69.988	79.54 ± .003	3	.787
64.812	46.19 ± .04	4	.784
59.894	26.85 ± .03	3	.782
54.967	15.30 ± .014	4	.777
49.974	8.473 ± .002	5	.772
44.872	4.475 ± .002	4	.767
39.995	2.370 ± .002	4	.760
35.038	1.206 ± .001	4	.752

<sup>a</sup> *n* is the number of parallel runs from which the average values of  $k_1$  is determined.

are given with the average deviation from the mean of *n* parallel runs. The temperature dependence of these rate data were fitted by a least squares calculation to the following empirical three constant equation

$$\log k = -10,000.619/T - 31.8624 \log T + 106.83054 \quad (2)$$

Deviations from this equation are of the order of the experimental variations found for the *n* individual rates at a single temperature and show no systematic variation which would suggest that further terms should be included. Since the deviations are small and random, the use of the above form of empirical equation seems justified even though some other equation might prove equally good.<sup>14</sup> Combining equations 1 and 2 gives the expression

$$\log k_{D_2O}/k_{H_2O} = -693.707/T - 4.4867 \log T + 13.29353 \quad (3)$$

from which the corresponding values of  $k_{D_2O}/k_{H_2O}$  for the experimental temperatures in Table I can be found. Clearly the change in  $k_{D_2O}/k_{H_2O}$  with temperature for a single compound is very similar to the trend shown through a series of halides of different reactivity, though the range of the variation is limited by the fact that the investigation was not extended below 35°. The value of  $k_{D_2O}/k_{H_2O}$  for 4° calculated from equation 3 is 0.677; the value found for *t*-butyl chloride at the same temperature was 0.695.<sup>15</sup> Reasoning from solubility characteristics,<sup>9</sup> we should have expected a lower value for the chloride unless some specific factor introduces small alterations in the ratios. Such specific differences which presumably contributed to the scatter in the halide ratios in our earlier publication<sup>3</sup> are eliminated here and hence a more detailed examination of the temperature dependence of the  $k_{D_2O}/k_{H_2O}$  ratio is possible.

The trend in  $k_{D_2O}/k_{H_2O}$  values (Table I) shows a significant temperature dependence in the range

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(15) P. M. Laughton and R. E. Robertson, *Can. J. Chem.*, **34**, 1714 (1956).

35–80° confirming the conclusion of Laughton and Robertson<sup>3</sup> but at variance with the conclusion of Swain and Bader<sup>5</sup> for temperatures above 18°. Their conclusion was based partially on non-kinetic evidence that the structural difference between the two media remains constant above this temperature. This conclusion seems very doubtful in view of our results and does not necessarily follow from the evidence cited by them. Thus the Baker viscosity relation<sup>16</sup> is applicable over a very restricted range of temperature, and its failure at lower and higher temperatures is consistent with a decreasing structural difference with increasing temperature. While the librational frequencies (Table I, ref. 5) they report show marked change between 10 and 25°, these results come from different laboratories and would be more convincing if there was one temperature in common with the earlier investigation of Giguère and Harvey.<sup>17</sup> If librational frequency contributes but 17% to the difference in heat content<sup>18</sup> and the heat capacity term for H<sub>2</sub>O and D<sub>2</sub>O show very small trends with temperature over the range of interest, then conclusions drawn from calculation of relative heat contents with respect to the temperature dependence of the structural difference are unconvincing. The question of whether there is a rapid change in relative structure (and hence in  $\delta_M F_S$ ) in the region 0–20° has not been explored here but indirect evidence weighs against such a conclusion. In our study of the hydrolysis of methyl benzenesulfonate<sup>12</sup>; isopropylbenzenesulfonate, tosylate and methanesulfonate<sup>10</sup>; and methanesulfonyl chloride and benzenesulfonyl chloride<sup>19</sup> there is no indication in  $d\Delta H^*/dT$  of a more rapid change in the structural stability of water at the lower temperatures. For these reasons we set aside the arguments advanced by Swain and Bader concerning  $d(k_{D_2O}/k_{H_2O})/dT$  and our earlier assumption<sup>4</sup> and proceed to examine the reasons why  $k_{D_2O}/k_{H_2O}$  might be expected to vary with temperature over the entire experimental range.

**Composition of the Solvent Isotope Effect in Hydrolysis.**—As a convenience for examining components of  $k_{D_2O}/k_{H_2O}$  the formal separation is made

$$\Delta F^* = (F^*_{R^+} + F^*_{X^-} + F^*_{I}) - (F_S + F_I)$$

where R<sup>+</sup> and X<sup>-</sup> refer to the solvent associated with the quasi-ions in the transition state, S to the solvent in the initial state solvation shell and I to the solute. The isotope effect due to a change in medium will be given by the difference indicated by the operator  $\delta_M$ , the assumption being made that  $\delta_M(\Delta F^*_{I^*} - \Delta F_I)$  is negligible. Strictly, the term  $\delta_M F^*_{R^+}$  includes not only solvent isotope effects but also any possible secondary deuterium isotope effects arising from differences in the O–H bond as a result of nucleophilic interaction. As we shall show presently, this factor is small, if not negligible, and the main source of the effect is still to be related to  $\delta_M F_S$  and this in turn to the rela-

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(19) R. E. Robertson, unpublished work.

tive difference in structural stability of the two media as suggested in our earlier papers.

The structural nature of water has been discussed repeatedly and no agreement appears to exist as to the exact description. Whether it approximates to the idealized tridymitic and quartz-like structure Bernal and Fowler<sup>20</sup> put forward as a working hypothesis<sup>21</sup> or the more recent polyhedra of Pauling<sup>22</sup> or the string-bag hypothesis of Pople with bendable hydrogen bonds<sup>23</sup> or the fluttering cluster theory of Frank and Wen,<sup>24</sup> it is sufficient for our purpose that relative structural stability be recognized as determining, to a large degree, the characteristics of aqueous solutions and differentially (equation 5) between D<sub>2</sub>O and H<sub>2</sub>O, providing a source of the solvent isotope effect. Since no general agreement has been reached as to which of the above hypotheses is preferable, it would seem premature as well as unnecessary to be more specific here, particularly when we must add to our considerations the further uncertainties attending initial and transition state solvation. Calculations based on an investigation of the temperature dependence of dielectric relaxation, viscosity and self-diffusion lead Saxton,<sup>25</sup> Collie, Hasted and Ritson<sup>26</sup> and Wang<sup>27</sup> to conclude that a common energy barrier of 4–5 kcal. was associated with the rate-controlling step in the disruption of water structure. Furthermore, in such physical processes, where the moment of inertia relating to rotation about the O–H axis is dominant,<sup>5, 28, 29</sup> D<sub>2</sub>O invariably shows evidence of greater structural stability than H<sub>2</sub>O. Thus Conway<sup>30</sup> calculated that ( $H^*_{D_2O} - H^*_{H_2O}$ ) for dielectric relaxation was 300 cal. and a similar value was to be expected<sup>31</sup> and was found for viscosity<sup>32</sup> based on data of Harday and Cottingham.<sup>6</sup> In both calculations,  $\Delta H^*$  was found to decrease with rising temperature with a coefficient of about –30 cal./deg. Since structural stability as used here is the physical consequence of the difference between structure forming from dipole–dipole interaction and the structure breaking of thermal activation; as the latter increases the residual must decrease both absolutely and differentially as between H<sub>2</sub>O and D<sub>2</sub>O whatever model of water we choose to adopt.

We have previously assumed the source of the solvent isotope effect to be associated with the double difference in relative initial state structural stability and here make the further assumption that the temperature dependence of  $k_{D_2O}/k_{H_2O}$ ,

illustrated in Table I, arises in the same way as  $d\Delta H^*/dT$  for the physical processes cited above if due allowance is made for differences associated with the changes in structure of water caused by the presence of solutes.

When a weakly polar molecule is dissolved in water, it creates asymmetry in the field of contiguous water molecules leading to a loss in librational freedom, *i.e.* an increased restriction to rotation about the O–H axis as a result of an increase in nearest neighbor water–water interaction. Indeed, the thermodynamic parameters characterizing this process are determined in the main by this increased water–water interaction rather than by water–solute interaction. The enthalpy of solvation is negative and decreases with temperature, *i.e.*, having large positive heat capacity values consistent with the description outlined above and discussed in greater detail by Eley,<sup>33</sup> Frank and Evans,<sup>34</sup> Glew and Moelwyn-Hughes,<sup>35</sup> Bohon and Claussen<sup>36</sup> and others.<sup>5, 28, 29</sup> If the solute contains centers providing a possibility for some degree of hydrogen bonding, then loss of librational freedom noted above as characterizing the formation of an aqueous solution of non-polar molecules will be reduced, the entropy will be less negative than for a less polar molecule and the heat capacity effect less positive. Obviously there is the possibility for a range of initial state solvation shells with varying stability characteristic of the polarity of the solute and as a corollary, with varying degrees of relative structural stability as between solvation by D<sub>2</sub>O and H<sub>2</sub>O. Thus the much stronger interaction between sulfonates and water compared with halides and water leads to corresponding reduction in the relative structural stability of the initial state solvation shells about the former. Solvation parameters for the halides<sup>9</sup> predict an increase in water–water interaction about isopropyl bromide relative to bulk water while the presence of more basic oxygen atoms in the sulfonate may lead to a decrease in structural stability in the initial state solvation shell compared to bulk water.

Laughton and Robertson concluded in an earlier paper<sup>4</sup> that such differences in stability of initial state solvation shell  $\delta_M F_S$  largely determine  $\delta_M \Delta F^*$ . This conclusion differed from that of Pritchard and Long<sup>37</sup> who assumed the major terms to be  $\delta_M F^*_{X^-}$  or of Swain, Cardinaud and Ketley<sup>38</sup> who expected  $\delta_M F^*_{R^+}$  to make important contributions to  $\delta_M \Delta F^*$ . From equation 5 our assumption requires that

$$\delta_M F_S \gg (\delta_M F^*_{X^-} + \delta_M F^*_{R^+}) \quad (6)$$

This requirement would appear to neglect such well known differences in solvent isotope effect for aqueous solutions of ions as shown by relative heats of solvation<sup>39</sup> and relative solubility in D<sub>2</sub>O

- (20) J. D. Bernal and E. Fowler, *J. Chem. Phys.*, **1**, 515 (1933).  
 (21) J. D. Bernal in "Hydrogen Bonding," edited by Hadzi, Pergamon Press, New York, N. Y., 1959, p. 6.  
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 (23) J. A. Pople, *Proc. Roy. Soc. (London)*, **A205**, 163 (1951).  
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 (36) R. F. Bohon and W. F. Claussen, *J. Am. Chem. Soc.*, **73**, 1571 (1951).  
 (37) J. G. Pritchard and F. A. Long, *ibid.*, **78**, 6008 (1956).  
 (38) C. G. Swain, R. Cardinaud and A. D. Ketley, *ibid.*, **77**, 934 (1955).  
 (39) E. Lange and W. Martin, *Z. phys. Chem.*, **A180**, 233 (1937).

and H<sub>2</sub>O.<sup>40</sup> In the latter, the solvent isotope effect appears to be of the same magnitude for ions and for some non-electrolytes in apparent conflict with the above inequality. The anomaly disappears when it is recognized that major contributing factors to this isotope effect may be related to initial state differences in the two bulk media. The factors determining  $k_{D_2O}/k_{H_2O}$  stem from the property of neutral molecules (the initial state, here) to increase the structural stability of the solvation shell relative to bulk media thus enhancing solvation differences while singly charged ions of intermediate size break down structure and so tend to reduce this difference. Bernal and Fowler<sup>18</sup> appear to have been among the first to recognize this property of ions to "raise the structural temperature" of water, a view subsequently supported by evidence from viscosity<sup>41,42</sup> infrared,<sup>5,43</sup> dielectric dispersion<sup>44</sup> and diffusion rates.<sup>28,45</sup> Even so, characteristic differences were observed with changing size and charge, in each physical parameter, and the fact that a greater degree of scatter in the  $k_{D_2O}/k_{H_2O}$  values was not observed in our survey of the alkyl halides<sup>3</sup> is consistent with inequality above.

If there is a charge of 0.8e or greater on the developing anion,<sup>9</sup> a similar charge must be associated with the cationic moiety or vicinity with a corresponding decrease in the structural stability of initial state solvation shell, and hence  $\delta_M F^*$  will be small compared with  $\delta_M F_s$ . Because there is ample evidence for differences in the degree of overlap between oxygen of water acting as a nucleophile and different alkyl groups for a given series<sup>13</sup> and for different displaced groups for the same alkyl group,<sup>46</sup> a corresponding variation in  $\delta_M F^*$  might be anticipated from a secondary deuterium isotope effect because of corresponding differences in the loosening of the O-H binding in the transition state. In Table II corresponding values of  $k_{D_2O}/k_{H_2O}$  for the hydrolysis of methyl and isopropyl esters are arranged in the order of increasing covalent bond formation in the transition state for the methyl compound. While the order

TABLE II

A COMPARISON OF SOLVENT ISOTOPE EFFECTS FOR METHYL AND ISOPROPYL COMPOUNDS HYDROLYZING IN WATER

Temp., °C.	60	60	90	80	80
Anion	Bzs.	Mes	Cl	Br	I
Methyl	0.905	0.94	0.78	0.81	0.816
Isopropyl	(0.94)	(0.94)	0.75	0.79	0.767

$k_{D_2O}/k_{H_2O}$  (isopropyl) >  $k_{D_2O}/k_{H_2O}$  (methyl) is consistent with a contribution to  $\delta_M F^*$  from a secondary isotope effect as noted above, this simple hypothesis would require an increasing difference

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(41) W. M. Cox and J. H. Wolfenden, *Proc. Roy. Soc. (London)*, **A145**, 475 (1934).

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(46) S. Hartman and R. E. Robertson, *Can. J. Chem.*, **38**, 2033 (1960).

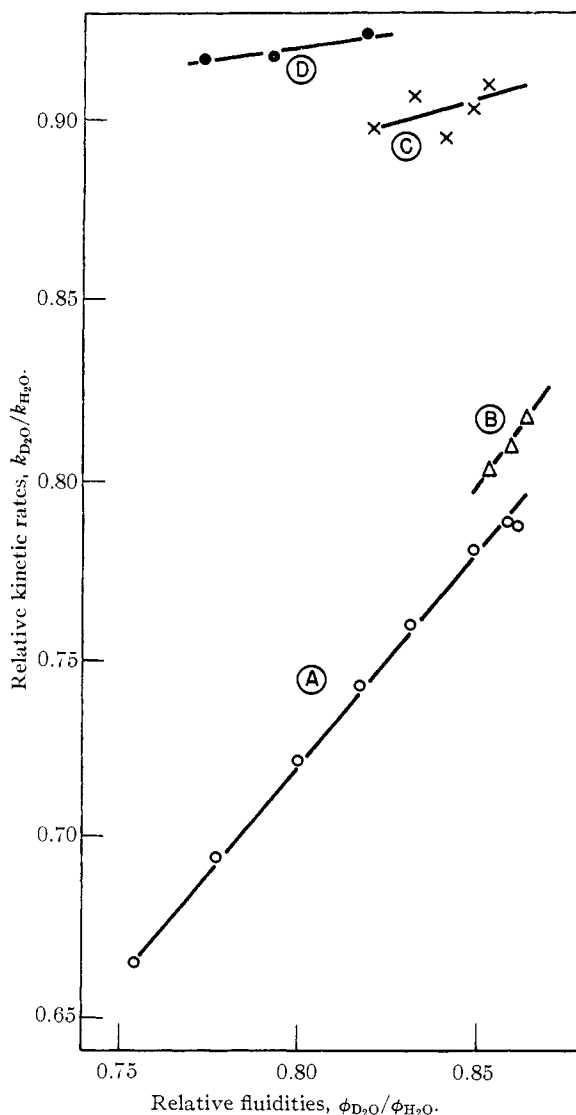


Fig. 1—A correlation of kinetic solvent isotope effects for the hydrolysis of a series of esters with the corresponding values for the relaxation process in bulk water: A, isopropyl bromide; B, methyl bromide; C, isopropyl benzenesulfonate; D, methyl benzenesulfonate.

of the same kind from left to right. No such trend is observed, hence we conclude that any contribution from this source is negligible.

**Temperature Dependence of  $\delta_M F^*$ .**—Since the evidence from studies of self-diffusion<sup>27,28</sup> dielectric-relaxation<sup>7,26,30</sup> and viscosity<sup>6</sup> cited above show that the structure of water decreases both absolutely and relatively in structure as between D<sub>2</sub>O and H<sub>2</sub>O with increasing temperature, the reasonable assumption from the above analysis is that, for a single compound,  $k_{D_2O}/k_{H_2O}$  will also vary with temperature either more or less than bulk water depending on the nature of the solute. The linear correlation obtained by plotting the  $k_{D_2O}/k_{H_2O}$  values of Table I against the relative fluidity values at corresponding temperatures calculated from the data of Harday and Cottington<sup>6</sup> (Fig. 1) provide striking support for this hypothesis. In the same plot are included a few values for methyl

bromide<sup>4</sup> and for methyl benzenesulfonate and isopropyl benzenesulfonate. The differences as well as similarities in the slopes of these plots are consistent with our assumptions.

The slope for isopropyl bromide (1.21) indicates a larger temperature coefficient for  $k_{D_2O}/k_{H_2O}$  than for the relaxation process in bulk water. This result is consistent with a higher energy barrier to rotation in the initial state solvation shell about the halide compared to bulk water (4–5 kcal.) and the implication of equation 6. Similar enhanced stability is indicated for the initial state solvation shell about methyl bromide<sup>9</sup> and hence a similar temperature dependence for  $k_{D_2O}/k_{H_2O}$  would be expected and is found.

The slope for the benzenesulfonates is obviously less than unity. The difference between this value and that for the halides is consistent both with the absolute difference in the magnitude of the solvent isotope effect already noted<sup>3,4</sup> and with the explanation advanced above. If the sulfonic oxygens provide competing centers for hydrogen bonding and thus increase the rotational freedom of contiguous water molecules, or, alternately, if the adjacent water molecules are more strongly hydrogen bonded to these sulfonic oxygens in the initial state, the solvent isotope effect and the temperature dependence thereof will be reduced. The latter hypothesis is probably more likely since the ability of sulfonic groups to confer greater solubility on many organic molecules is well known. The close parallel between the differences in the temperature dependence of the solvent isotope effect for halides and sulfonates noted above and the corresponding differences in the heat capacity of activation for hydrolysis,  $\Delta C_p^*$ , may also be

traced to this common source—the difference in the initial state solvation shells.

**Derived Thermodynamic Parameters.**—If the usual assumptions are made concerning equilibrium between the initial and transition states and further we assume that  $dC_p^*/dT = 0$ ,<sup>12</sup> then from the empirical constants of equation 2, the derived parameters characterizing the activation process may be calculated. These are collected in Table III along with the corresponding terms from the hydrolysis of isopropyl bromide in  $H_2O$ .

TABLE III  
A COMPARISON OF THERMODYNAMIC PARAMETERS FOR THE ACTIVATION PROCESS IN THE HYDROLYSIS OF ISOPROPYL BROMIDE IN  $H_2O$  AND  $D_2O$

Temp., °C.	In $H_2O$ <sup>a</sup>		In $D_2O$ <sup>b</sup>	
	$\Delta H^*$ , cal./mole	$\Delta S^*$ , cal./mole deg.	$\Delta H^*$ , cal./mole	$\Delta S^*$ , cal./mole deg.
0	27,180	8.05	27,920	9.94
50	24,360	-1.43	24,670	-1.03
100	21,540	-9.54	21,390	-10.43

<sup>a</sup>  $\Delta C_p^* = -56.4$  cal./mole deg.    <sup>b</sup>  $\Delta C_p^* = -65.3$  cal./mole deg.

Since qualitative arguments lead to the conclusion that the major contribution to  $\Delta C_p^*$  is  $dF_s/dT$ , it is gratifying to discover that there is a significant difference between  $\Delta C_p^*(D_2O)$  and  $\Delta C_p^*(H_2O)$  and the values of both terms are more negative than that calculated by Conway<sup>30</sup> and ourselves<sup>32</sup> for the relaxation processes in bulk water. The differences between  $\Delta H^*$  and  $\Delta S^*$  for the two media may likewise be interpreted as reflecting the greater stability of the initial state solvation shell in  $D_2O$  than in  $H_2O$ .

[CONTRIBUTION FROM MELLON INSTITUTE, PITTSBURGH, PENNSYLVANIA]

## <sup>13</sup>C Nuclear Magnetic Resonance Spectroscopy. I. Aromatic Hydrocarbons

BY PAUL C. LAUTERBUR<sup>1</sup>

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The <sup>13</sup>C nuclear magnetic resonance spectra of benzene, toluene, the three xylenes, mesitylene, durene and hexamethylbenzene, and of biphenyl, naphthalene, phenanthrene, pyrene, acenaphthylene and fluoranthene have been obtained and partially analyzed. Tentative assignments for the spectra of azulene and 4,6,8-trimethylazulene are also presented. The ranges of <sup>13</sup>C chemical shifts in non-alternate hydrocarbons are much larger than those observed in alternates, suggesting that variations in  $\pi$ -electron densities are primarily responsible for such shifts in aromatic rings.

### Introduction

The <sup>13</sup>C nuclear magnetic resonance (n.m.r.) spectra of several series of substituted benzenes and heterocyclic aromatics have been obtained and analyzed. The analyses of the complex spectra were usually accomplished by comparisons among the spectra of the methyl derivatives, a procedure made possible by the relatively small effects of methyl substitution on <sup>13</sup>C shifts and carbon-hydrogen spin-spin couplings in aromatic ring systems. The interpretation of the measured <sup>13</sup>C shifts and carbon-hydrogen spin-spin couplings depends initially upon the establish-

ment of empirical correlations with more familiar chemical and physical parameters. This paper, the first of a series on the <sup>13</sup>C n.m.r. spectra of aromatic rings, therefore presents measurements and analyses of the spectra of benzene and seven methylbenzenes, and of biphenyl, three alternate and four non-alternate hydrocarbons. Deuteration of two of the latter, azulene and 4,6,8-trimethylazulene, in the 1,3 positions has made possible a tentative analysis of their spectra, from which it appears that the <sup>13</sup>C shifts may be determined largely by the  $\pi$ -electron density distribution in such molecules.

The spectrum of ferrocene has also been obtained. The <sup>13</sup>C resonance occurs at much higher

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