COMMUNICATIONS TO THE EDITOR

THERMAL PROPERTIES OF ISOPENTANE[1]

Sir:

Several years ago some work from the Cryogenic Laboratory of this School[2,3,4] reported hysteresis effects in the determination of the liquid heat capacities and vapor pressures of isopentane (2-methylbutane). This effect was attributed to a slow change with temperature of the rotational isomeric composition of the liquid. Guthrie and Huffman[5] did not observe such effects in their independent determination of the heat capacities of this hydrocarbon.

It was decided to postpone further work on the heat capacity until this compound was investigated as part of a contemplated study of rotational isomerism by means of Raman spectroscopy in the Department of Physics of this School. The Raman spectroscopic study of this compound over a range of temperatures has now been completed.[6] In the course of this work the relative intensity changes of two Raman lines, assumed to be caused by a change in the rotational isomeric composition of the liquid, were measured over the temperature range 310–120°K. If the above-mentioned hysteresis effects were real it would be expected that they might be observable in this experiment, *i. e.*, different results should be obtained for the relative concentration of the isomers, and therefore of the line–pair intensity ratio, at the lower temperature by slow and fast cooling of the sample. In order to investigate this point the line–pair ratio at low temperature was determined (a) after cooling from room temperature to the lower temperature in approximately ten minutes, and (b) after cooling gradually down to the low temperature over a period of five and a half hours. In both cases the line–pair ratio measured was identical within experimental error, *i. e.*, no hysteresis effects were observed.

Although the interpretation of the spectroscopic results with respect to rotational isomerism is not unequivocal,[5] the absence of any observable hysteresis suggests that the results and conclusions of Guthrie and Huffman are essentially correct.

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[1] This Research was supported by contract N6onr-269, Task V, of the Office of Naval Research.

[2] J. G. Aston and S. C. Schumann, This Journal, **64**, 1034 (1942).

[3] S. C. Schumann, J. G. Aston and M. L. Sagenkahn, *ibid.*, **64**, 1039 (1942).

[4] J. G. Aston, *ibid.*, **65**, 2041 (1943).

[5] A. B. Guthrie, Jr., and H. M. Huffman, *ibid.*, **65**, 1143 (1943).

[6] G. J. Szasz and N. Sheppard, *J. Chem. Phys.*, to be published.

WATER ACTIVITY CORRELATION IN THE HYDROCHLORIC ACID AZEOTROPIC SYSTEM

Sir:

In a recent paper[1] Stokes and Robinson attempted to extend the concepts of the Brunauer, Emmett and Teller adsorption theory to the case of ionic hydration in concentrated aqueous solution. They were able to show that the available data on water activity in several concentrated electrolytes were remarkably well fitted with reasonable values for the parameters in the following equation

$$\frac{ma_{\text{W}}}{55.51\,(1 - Ka_{\text{W}})} = \frac{1}{cKr} + \frac{c-1}{cr}\,a_{\text{W}}$$

where m is the molality of electrolyte; a_{W} is the activity of water; r, c and K are dimensionless parameters related to the number of water molecules in a monomolecular hydration layer when complete, the heat of adsorption of the first layer and of subsequent layers, respectively. In particular, the data from e. m. f. measurements on hydrochloric acid[2] in the range 0–50° were fitted with an average deviation of 0.0016 in a_{W} using the parameters $r = 4.00$, $RT \ln c = 1.57 \pm 0.01$ kcal.; $K = 0.825$ to 0.870.

It occurred to the present author that a further test of the validity of the theory would be afforded by data in a higher range of temperature, available in the form of accurate measurements of the azeotropic composition and total pressure of aqueous hydrochloric acid.[3]

The exact thermodynamic equation $a_{\text{W}}f^0_{(1)} = N_{\text{W}}f^0_{(g)}$, was applied to the calculation of water activity in the azeotropic mixtures. The use of fugacities (from Dorsey's data[4]) rather than the corresponding pressures introduced corrections of about 0.5%. The activities so calculated are believed to be correct within 0.0010 in a_{W}.

Table I

Water Activity in Azeotropic Hydrochloric Acid Systems

Temp., °C.	Mm.	N HCl	m HCl	a_{W}
90	366.7	0.11712	7.3633	0.617_8
100	548.3	.11692	7.1819	$.639_8$
110	799.8	.11088	6.9210	$.665_4$
120	1119	.10700	6.6514	$.675_2$

Choosing the parameters $r = 4.00$ and $RT \ln c = 1.57 \pm 0.01$ kcal., the present data were fitted (average deviations 0.0008 in a_{W}) by values of

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[1] R. H. Stokes and R. A. Robinson, This Journal, **70**, 1870 (1948).

[2] G. Akerlof and J. W. Teare, This Journal, **59**, 1855 (1937).

[3] W. D. Bonner and R. E. Wallace, *ibid.*, **52**, 1747 (1930).

[4] N. E. Dorsey, "Properties of Ordinary Water Substance," Reinhold Publishing Corporation, New York, N. Y., 1940, pp. 576, 596.

K = 0.841, 0.832, 0.825, 0.837 and 90, 100, 110 and 120°, respectively. The agreement between the high and low temperature results is all that can be desired in view of the somewhat vague nature of the parameter K; thus the theory appears to be in accord with facts in a hitherto untested region.

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A NEW SYNTHESIS OF SULFONYL CHLORIDES

Sir:

It has been established in previous publications from this Laboratory[1] that under certain conditions sulfuryl chloride is a useful reagent for the chlorination and sulfonation of saturated hydrocarbons, and for the addition of chlorine to olefins to produce dichloro compounds.[2] In the preparation of the dichloro derivatives from the olefins and sulfuryl chloride, the suggested procedure was to mix equimolecular quantities of the reactants, and a small quantity (1–2 mole per cent.) of a diacyl peroxide and to heat the mixture.

We now find that if to the mixture of the olefin and the diacyl peroxide (1–2 mole per cent.) maintained at 60–70°, sulfuryl chloride (dissolved in the olefin) is added dropwise, there is formed besides the dichloro derivative a considerable quantity of a compound containing two molecular equivalents of the olefin to one of the sulfuryl chloride, as well as some other, as yet unidentified, products.

A mixture of octene-1 (45 g.) and dibenzoyl peroxide (2 g.) is heated to 60°, and sulfuryl chloride (30 g.), dissolved in octene-1 (50 g.), is added dropwise over a period of six hours, while a slow stream of sulfur dioxide is passed through the reaction mixture. The heating is continued for two hours longer. Distillation of the reaction mixture gave 13 g. of dichloroöctane (b. p. 67–71° (4 mm.), n^{20}_{D} 1.4531, Cl 38.38%, mol. wt. 183) and a residue. The major part of this residue sublimed readily when heated to 110–140° (10^{-5} mm.). When crystallized from alcohol a white crystalline material (22 g.) was obtained which melted at 57–58°.

Anal. Calcd. for $C_{16}H_{32}O_2SCl_2$: Cl, 19.73; mol. wt., 359.4; neut. eq., 179.7. Found: Cl, 19.58, 19.67; mol. wt., 365; neut., eq., 180.

The formation of the compound $C_{16}H_{32}O_2SCl_2$ from octene-1, sulfuryl chloride and a small amount of benzoyl peroxide, probably proceeds as follows

$$SO_2Cl_2 + \xrightarrow{(C_6H_5COO)_2} C_6H_5Cl + \cdot SO_2Cl \qquad (1)$$

$$\cdot SO_2Cl \longrightarrow SO_2 + Cl\cdot \qquad (2)$$

$$n\text{-}C_6H_{13}CH{=}CH_2 + Cl\cdot \longrightarrow ClCH_2(n\text{-}C_6H_{13})CH\cdot \qquad (3)$$

$$\underset{\text{(A)}}{ClCH_2(n\text{-}C_6H_{13})CH\cdot + n\text{-}C_6H_{11}CH{=}CH_2 \longrightarrow n\text{-}C_6H_{13}[ClCH_2(n\text{-}C_6H_{13})CHCH_2]CH\cdot} \qquad (4)$$

$$(A) + SO_2 \longrightarrow ASO_2\cdot \qquad (5)$$

$$(B) + SO_2Cl_2 \longrightarrow n\text{-}C_6H_{13}CH(SO_2Cl)CH_2CH(CH_2Cl)n\text{-}C_6H_{13} + \cdot SO_2Cl \qquad (6)$$

The analyses, molecular weight, neutralization equivalent, and the fact that the compound is soluble in sodium hydroxide and is not subsequently precipitated by acid, indicate that the compound is a sulfonyl chloride and not a chlorinated sulfone.

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[1] Kharasch and Brown, THIS JOURNAL, **61**, 2142 (1939); **61**, 3432 (1939); **62**, 925 (1940); Kharasch and Read, **61**, 3089 (1939).

[2] The original papers should be consulted for the mechanisms of these reactions.

ULTRAVIOLET SPECTRUM OF FLUORINATED BENZENES

Sir:

The spectra of fluorinated benzenes and toluenes have been measured in the 1700–2800 Å. region. Because of the current interest in fluorocarbons, we present a preliminary comparison of the spectra of perfluorotoluene[1] (b. p. 103.5°) and toluene (API-NBS)[2] in n-heptane solution in Table I, where ϵ is the molecular extinction coefficient and f the oscillator strength.

TABLE I

MAIN FEATURES OF SPECTRA

	Toluene	Perfluorotoluene
$^1A_{1g}$–$^1B_{2u}$ type forbidden transition		
Onset	37,300	near 36,800 cm.$^{-1}$
$\epsilon_{\max}$	230	1,080
f	0.004	0.021
$^1A_{1g}$–$^1B_{1u}$ type forbidden transition		
Onset	46,300	near 47,500
$\epsilon_{\max}$	8,100	7,000
f	0.12	0.12
$^1A_{1g}$–$^1E_{1u}$ type allowed transition		
Peak	53,000	56,100
$\epsilon_{\max}$	55,000	48,000
Total f	1.09	0.91

The previously studied simple substituents on benzene, such as alkyls, halides, etc., which do not conjugate with the ring, cause little change in the position of the 2600 Å. forbidden transition ($^1A_{1g}$–$^1B_{2u}$). They cause some red shift in the 2100 Å. forbidden transition ($^1A_{1g}$–$^1B_{1u}$), and larger red shifts in the allowed 1835 Å N → V ($^1A_{1g}$–$^1E_{1u}$) transition.[2] Increasing shifts in the shorter wave length bands are noted here except that they are in the opposite direction, *i. e.*, "toward the blue." Saturated fluorocarbon spectra show blue shifts compared to the corresponding hydrocarbon as seen in the extension of solu-

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[1] Kindly supplied by Dr. E. T. McBee.

[2] J. R. Platt and H. B. Klevens, *Chem. Rev.*, **41**, 301 (1947).