

the fluorochlorates, BrF_3 from the fluorobromates and IF_5 from the fluoriodates. The order of stability seems to be $\text{Cs} > \text{Rb} > \text{K}$. The order of reactivity with water is $\text{Cl} > \text{Br} > \text{I}$.

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MOLAR REFRACTION AS AN INDEX OF PROTON TRANSFER: AN ESTIMATE OF THE ACID STRENGTH OF *p*-TOLUENESULFONIC ACID

Sir:

p-Toluenesulfonic acid is strong in water but largely un-ionized in 100% sulfuric acid.¹ We

medium effects for salts or strong acids even up to rather high ionic concentrations.⁵⁻⁸ Thus, if we ascribe the medium effect on *R* entirely to proton transfer, the ratio $c_{\text{C}_7\text{H}_7\text{SO}_3^-}/c_{\text{C}_7\text{H}_7\text{SO}_3\text{H}}$ is unity at about 43 wt. % H_2SO_4 . Using this datum, we could estimate pK_A of *p*-toluenesulfonic acid if the appropriate acidity function, H_- , were known.⁹ Unfortunately, this function is not known for arylsulfonic acids in 43 wt. % H_2SO_4 . We may, however, approximate its value by using recent data for the ionization of nitric acid,^{10,11} as shown in equation (1). On this basis, pK_A for *p*-toluenesul-

$$pK_A(\text{C}_7\text{H}_7\text{SO}_3\text{H}) = pK_A(\text{HNO}_3) + \left[\log \left(\frac{c_{\text{NO}_2^-}}{c_{\text{HNO}_3}} \right) \right]_{43\% \text{H}_2\text{SO}_4} \quad (1)$$

fonic acid is estimated as -1.3 at 25° . For comparison, pK_A for methanesulfonic acid has been

TABLE I
DATA AT 25.0°

Wt. % H_2SO_4	d_0	n_D^{20} ^{a,b}	$10^3 K_d$	$10^3 K_n$ ^a	<i>R</i> (cc./mole)
0	0.997075	1.33256	72.1 ± 0.2	32.04 ± 0.10	43.11 ± 0.06
20	1.13647	1.35611	45.9 ± 0.2	$26.61 \pm .15$	$43.21 \pm .09$
40	1.29906	1.38069	17.9 ± 0.2	$20.30 \pm .27$	$42.50 \pm .16$
60	1.49398	1.40632	-12.0 ± 2.0	$14.69 \pm .24$	$41.75 \pm .39$
80	1.7216	1.43280	-43.4 ± 1.5	$10.58 \pm .16$	$41.39 \pm .30$

^a Refractive index data for the helium D_3 line, 5870 Å. ^b By interpolation from data of reference 5.

have measured the apparent molar refraction, *R*, of sodium *p*-toluenesulfonate in sulfuric acid-water mixtures, in the hope that proton transfer from the medium might be detected by a characteristic reduction in \bar{R} .^{2,3}

Experimental values of several functions of the solvent composition are listed in Table I: the solvent density, d_0 ; the refractive index, n_0 ; the initial slopes, $K_d = (d - d_0)/c$ and $K_n = (n -$

estimated recently as -0.6 by a quite different method.¹²

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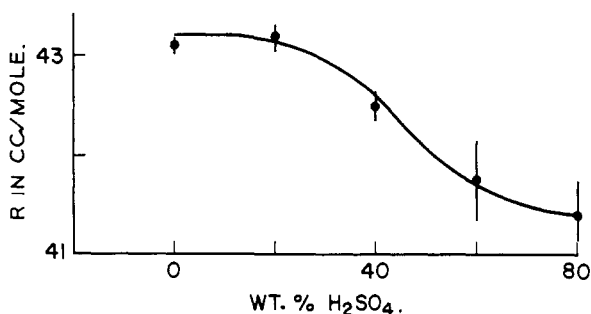


Fig. 1.—Apparent molar refraction of sodium *p*-toluenesulfonate vs. wt. % H_2SO_4 ; data at 25° .

$n_0)/c$, where c is the formal concentration of sodium *p*-toluenesulfonate; and *R*, computed from these quantities in the standard way.⁴ The plot of *R* vs. wt. % H_2SO_4 has an inflection at about 43 wt. %, as shown in Fig. 1.

The relatively large decrease in the value of *R* and particularly the inflection are almost certainly the result of proton transfer, since such behavior has no analogy in any of the previously published

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MOLECULAR GEOMETRY AND THE VAPOR PRESSURE OF ISOTOPIC MOLECULES. THE EQUIVALENT ISOMERS *cis*-, *gem*- AND *trans*-DIDEUTERIOETHYLENES¹

Sir:

We wish to report a difference in vapor pressure of isotopic molecules which is associated with molecular geometry. The vapor pressure of *trans*-dideuterioethylene has been found to be larger than that of either *cis*- or *gem*-dideuterioethylene. Initial experiments were made in an efficient packed column of about 80 plates on mixtures of *cis*- and *trans*-dideuterioethylene, monodeuterioethylene and ethylene. These results now have been confirmed and extended by manometric measurements over the temperature range 130 – 180°K . on highly purified samples. The samples were purified by low temperature gas chromatography and contained less than 10^{-2} mole per cent. chemical impurities.

(1) Research carried out under the auspices of the U. S. Atomic Energy Commission.

The dideuterioethylenes were geometrically pure and contained less than 2 per cent. monodeuterioethylene.

The vapor pressures of *cis*- and *gem*-dideuterioethylene are equal to within a few hundredths of a per cent. The *trans* compound value is greater than either the *cis* or the *gem* by 0.1% at the low temperatures and 0.05% at 180°K. The vapor pressure of *trans*-dideuterioethylene is 1.2% greater than that of ethylene at 130°K. and 1.6% greater at 180°K.

The existence of a difference between the equivalent structural geometric isomers, *cis*-, *trans*- and *gem*-dideuterioethylenes, the larger vapor pressure of the dideuterio compounds, and the largest pressure for the *trans*-dideuterioethylene support the structural theory of vapor pressure of isotopic molecules.² In the theory, a difference in the first quantum effect $(h/kT)^2$ between non-equivalent isotopic isomers, e.g., $N^{15}N^{14}O^{16}$ and $N^{14}N^{15}O^{16}$ was predicted and found.³ No such difference is to be expected in this approximation between equivalent isotopic isomers. The difference between the equivalent isomers can be interpreted in terms of quantum effects of the order $(h/kT)^4$ or in terms of the zero point energy difference of the liquid and gas. Both descriptions are equivalent and confirm a decrease in the C-H molecular stretching frequencies on condensation.⁴ The facts that the dideuterioethylenes are but 1.5% more volatile than ethylene and the *trans* is the most volatile is a consequence of stiffening of planar and out of plane bending motions of the hydrogen atoms by the intermolecular forces. The mathematical theory can be phrased as follows: condensation favors the clustering of deuterium within the molecule. This explanation is further confirmed by the difference in temperature coefficients of P_{trans}/P_{cis} vs. P_{trans}/P_{ord} .

A detailed description of the experiments and a full exposition of the applicable theory will be submitted for publication shortly.

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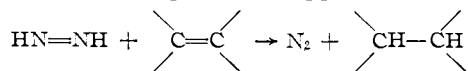
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CHEMISTRY OF DIIMIDE. II. STEREOCHEMISTRY OF HYDROGEN TRANSFER TO CARBON-CARBON MULTIPLE BONDS

Sir:

In Part I¹ we have proposed that diimide (HN=NH) is the active hydrogenator in the reduction of unsaturated linkages by mixtures of hydrazine and oxidizing agents such as oxygen-copper ion and hydrogen peroxide-copper ion



Of special note are the following points:

(1) E. J. Corey, W. L. Mock and D. J. Pasto, *Tetrahedron Letters*, **11**, 353 (1961); see also S. Hünig, H. Müller and W. Thier, *ibid.*, in press (1961).

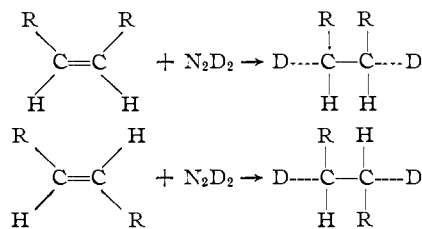
1. Reduction of multiple bonds also can be effected by decarboxylation of potassium azodiformate (KOOCN=NCOOK) in aqueous media, a process which quite clearly involves the formation of diimide.²

2. Diimide itself possesses a finite lifetime; its decomposition into N_2 and H_2 appears not to be inevitable, and is probably even less favorable than intermolecular hydrogen transfer as exemplified by self-annihilation giving molecular nitrogen and hydrazine.^{2,3}

3. Diimide has been implicated^{4,5} as an intermediate in the oxidation of hydrazine by reagents such as are effective for hydrogenation of multiple bonds with hydrazine.

We now report that the steric course of this remarkable addition of hydrogen is *quite generally cis*, a finding in accord with the behavior expected of a hydrogenating agent which derives its reactivity from formation of a very stable molecule after the transfer of a pair of hydrogens.

The reduction of maleic and fumaric acids either by deuteriohydrazine-oxidizing agent or by potassium azodiformate-deuterium oxide affords stereospecifically *meso*- and *dl*-2,3-dideuteriosuccinic acids, respectively. The deuteriated succinic acids were assayed by infrared analysis, being readily distinguished by their markedly different absorption in the 8-9 μ region⁶; only the product of *cis*-addition was detectable and we estimate that these reductions are at least 97% stereospecific.



Similarly, reduction of *cis*- and *trans*-2-butene-1,4-diols produced only *meso*- and *dl*-2,3-dideuterio-butane-1,4-diols, respectively, isolated (after permanganate oxidation) and analyzed as the corresponding succinic acids.

Reduction of *cis*- and *trans*-stilbenes was also stereospecific in the deuteriated system, affording *meso*- and *dl*-1,2-dideuterio-1,2-diphenylethanes respectively. The stereochemistry of these deuteriated ethanes was determined by ozonolysis and oxidation to the succinic acids.

cis-Hydrogenation also was observed in the reaction of dimethylmaleic acid with hydrazine-hydrogen peroxide which afforded only *meso*-2,3-dimethylsuccinic acid. Further, reduction of acetylenic linkages also appears to be a *cis* addition. Partial hydrogenation of diphenylacetylene gave a mixture of starting material, *cis*-stilbene and 1,2-diphenylethane; no *trans*-stilbene could be isolated or detected by infrared analysis.

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