

tioned, was produced in detectable amount at any time during the reaction.

The same isomerization can be effected equally well using bicycloheptadiene-iron tricarbonyl (I), cyclooctatetraene-iron tricarbonyl or hexadiene-iron tricarbonyl in place of  $\text{Fe}(\text{CO})_5$ . It is significant, however, that the reaction did not occur when 1,3-cyclohexadiene-iron tricarbonyl was used. Furthermore, no rearrangement of 1,5-cyclooctadiene has been observed using  $\text{Mo}(\text{CO})_6$ ,  $\text{Cr}(\text{CO})_6$ ,  $\text{Ni}(\text{CO})_4$ ,  $\text{W}(\text{CO})_6$  or methylcyclopentadienylmanganese tricarbonyl, although several of these compounds are reported to form stable 1,5-cyclooctadiene metal carbonyl complexes.<sup>3</sup>

Reaction of  $\text{Fe}(\text{CO})_5$  with other non-conjugated dienes also has effected isomerization of the double bonds to produce conjugated systems, but in most of these cases the product is found to be a stable diene-iron tricarbonyl derivative. Thus, reaction of  $\text{Fe}(\text{CO})_5$  and 1,4-cyclohexadiene produced 1,3-cyclohexadiene-iron tricarbonyl, identical with that formed from reaction of 1,3-cyclohexadiene and  $\text{Fe}(\text{CO})_5$ . Similarly, 1,5-hexadiene and  $\text{Fe}(\text{CO})_5$  reacted to produce a mixture of 1,3-hexadiene- and 2,4-hexadiene-iron tricarbonyls. Reactions of  $\text{Fe}(\text{CO})_5$  with 4-vinylcyclohexane and *d*-limonene have led to the formation of mixtures of diene-iron tricarbonyl compounds. In each case it has been established, by degradation of the complexes, that the organic ligands in these mixtures are dienes isomeric with the starting materials; determination of the exact composition and structural nature of these mixtures is in progress. It should be noted that Stone and co-workers recently have obtained 1,3-pentadiene-iron tricarbonyl after reaction of 1,4-pentadiene with tri-iron dodecacarbonyl.<sup>4</sup>

Further work dealing with the mechanism and general applicability of this reaction will be reported in full in THIS JOURNAL. We thank the Robert A. Welch Foundation and Alfred P. Sloan Foundation for financial assistance.

(3) E. O. Fischer and W. Frohlich, *Ber.*, **92**, 2995 (1959); M. A. Bennett and G. Wilkinson, *Chemistry and Industry*, 1516 (1959); T. A. Manuel and F. G. A. Stone, *J. Am. Chem. Soc.*, **82**, 366 (1960).

(4) R. B. King, T. A. Manuel and F. G. A. Stone, *J. Inorg. and Nucl. Chem.*, **16**, 233 (1961).

DEPARTMENT OF CHEMISTRY  
UNIVERSITY OF TEXAS  
AUSTIN 12, TEXAS

J. E. ARNET  
R. PETTIT

RECEIVED JUNE 1, 1961

#### TETRAFLUROHALATES OF CESIUM, RUBIDIUM AND POTASSIUM<sup>1</sup>

Sir:

The interaction of elementary fluorine with  $\text{CsCl}$ ,  $\text{RbCl}$  or  $\text{KCl}$  results in the formation of powerful fluorinating agents. These compounds were first investigated by Bode and Klesper who claimed that the compound formed was  $\text{MF}_x$  where  $x$  approaches 3.<sup>2</sup> They reported that fluorination of  $\text{CsF}$ ,  $\text{RbF}$  and  $\text{KF}$  did not produce the "trifluorides" (we concur). These workers claimed

(1) The Los Alamos work was performed under the auspices of the U. S. Atomic Energy Commission and the University of Wisconsin work was supported by the Wisconsin Alumni Research Foundation, the du Pont Company, and the Monsanto Chemical Company.

(2) H. Bode and E. Klesper, *Z. anorg. allg. Chem.*, **267**, 97 (1951).

that it was necessary to start with the alkali chloride, arguing that the molecular volume of the chloride was just the right size to accommodate  $\text{F}_3^-$  when  $\text{Cl}^-$  was replaced. *Contrary to the previous work, we find that fluorination of alkali chlorides produces alkali tetrafluorochlorates,  $\text{MClF}_4$ , and not the trifluoride,  $\text{MF}_3$ .* Our results can be explained by the reaction  $\text{MCl} + 2\text{F}_2 = \text{MClF}_4$ .

Fluorination of the alkali halides ( $\text{CsCl}$ ,  $\text{CsBr}$ ,  $\text{CsI}$ ,  $\text{RbCl}$ ,  $\text{RbBr}$ ,  $\text{RbI}$ ,  $\text{KCl}$ ,  $\text{KBr}$  and  $\text{KI}$ ) at temperatures of 15–250° yields primarily the alkali polyfluorohalate. Pure polyfluorohalates are difficult to prepare since the reaction is very exothermic and the decomposition temperature is locally exceeded so that the product usually contains some alkali fluoride. The product occurs as a dense melt.

The most thoroughly studied of these compounds are potassium tetrafluorochlorate and cesium tetrafluorochlorate. These have been prepared by direct fluorination of the alkali chlorides at temperatures from 90–250°. These compounds are white, low melting (*circa* 100–200°) solids which react violently with water to yield primarily chlorate ion rather than chloride (this probably explains the failure of Bode and Klesper to find  $\text{Cl}^-$ ). They also oxidize iodide to iodine and evolve oxygen from the oxidation of water. They decompose to the alkali fluoride and gaseous products upon heating to 350–400° *in vacuo* or in an inert gas stream. The gases evolved upon thermal decomposition of  $\text{CsClF}_4$  are  $\text{ClF}$  and  $\text{ClF}_3$ .

X-Ray powder studies of these tetrafluorochlorates show a mixture of the alkali fluoride and a new phase resembling closely, but not exactly, the alkali perchlorate. Infrared absorption bands of  $\text{KClF}_4$ , both in  $\text{KCl}$  discs and in mulls, were found at 1970, 1830, 1225 and 970  $\text{cm}^{-1}$ . Magnetic susceptibility studies of  $\text{CsClF}_4$  show it to be diamagnetic.

The cesium product was analyzed by oxidation of  $\text{I}^-$  to  $\text{I}_2$ , by weight change occurring on fluorination, and by determination of the total chloride by precipitation of silver chloride after reduction of the chlorate with  $\text{Na}_2\text{SO}_3$ . The potassium salt was analyzed by iodine titration, by weight loss on heating and by fluoride determination with thorium nitrate.

Bode reported the preparation of strongly oxidizing salts from the fluorination of the alkali bromides and iodides as well as the chloride but did not characterize the products.<sup>3</sup> We have prepared the tetrafluorobromates and tetrafluoroiodates of  $\text{Cs}$ ,  $\text{Rb}$ , and  $\text{K}$ . The compound  $\text{CsBrF}_4$  was obtained almost completely free of  $\text{CsF}$ . There is some evidence for the existence of  $\text{CsIF}_6$ . The rubidium compounds have been studied and the compositions have been determined to be  $\text{RbClF}_4$ ,  $\text{RbBrF}_4$  and  $\text{RbIF}_4$ . The potassium compounds are more difficult to prepare in high yield with particular difficulty arising with  $\text{KI}$ .  $\text{KBrF}_4$  has been reported.<sup>4</sup>

Infrared examination of the gases evolved upon thermal decomposition show  $\text{ClF}$  and  $\text{ClF}_3$  from

(3) H. Bode, *Naturwiss.*, **37**, 477 (1950).

(4) A. G. Sharpe and H. J. Emeléus, *J. Chem. Soc.*, 2135 (1948), and A. A. Woolf and H. J. Emeléus, *ibid.*, 2865 (1949).

the fluorochlorates,  $\text{BrF}_3$  from the fluorobromates and  $\text{IF}_5$  from the fluoriodates. The order of stability seems to be  $\text{Cs} > \text{Rb} > \text{K}$ . The order of reactivity with water is  $\text{Cl} > \text{Br} > \text{I}$ .

LOS ALAMOS SCIENTIFIC LABORATORY  
LOS ALAMOS, NEW MEXICO  
DEPARTMENT OF CHEMISTRY  
UNIVERSITY OF WISCONSIN  
MADISON, WISCONSIN

L. B. ASPREY  
JOHN L. MARGRAVE  
MERLIN E. SILVERTHORN

RECEIVED JUNE 2, 1961

**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.<sup>1</sup> We

medium effects for salts or strong acids even up to rather high ionic concentrations.<sup>5-8</sup> 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. %  $\text{H}_2\text{SO}_4$ . Using this datum, we could estimate  $pK_A$  of *p*-toluenesulfonic acid if the appropriate acidity function,  $H_-$ , were known.<sup>9</sup> Unfortunately, this function is not known for arylsulfonic acids in 43 wt. %  $\text{H}_2\text{SO}_4$ . We may, however, approximate its value by using recent data for the ionization of nitric acid,<sup>10,11</sup> 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  $25^\circ$ . For comparison,  $pK_A$  for methanesulfonic acid has been

TABLE I  
DATA AT  $25.0^\circ$

Wt. % $\text{H}_2\text{SO}_4$	$d_0$	$n_D^{20}$ <sup>a,b</sup>	$10^3 K_d$	$10^3 K_n$ <sup>a</sup>	<i>R</i> (cc./mole)
0	0.997075	1.33256	$72.1 \pm 0.2$	$32.04 \pm 0.10$	$43.11 \pm 0.06$
20	1.13647	1.35611	$45.9 \pm 0.2$	$26.61 \pm .15$	$43.21 \pm .09$
40	1.29906	1.38069	$17.9 \pm 0.2$	$20.30 \pm .27$	$42.50 \pm .16$
60	1.49398	1.40632	$-12.0 \pm 2.0$	$14.69 \pm .24$	$41.75 \pm .39$
80	1.7216	1.43280	$-43.4 \pm 1.5$	$10.58 \pm .16$	$41.39 \pm .30$

<sup>a</sup> Refractive index data for the helium  $D_3$  line, 5870 Å. <sup>b</sup> 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  $\bar{R}$ .<sup>2,3</sup>

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  $K_n = (n -$

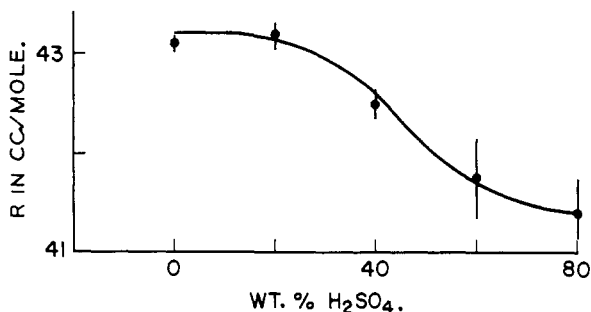


Fig. 1.—Apparent molar refraction of sodium *p*-toluenesulfonate vs. wt. %  $\text{H}_2\text{SO}_4$ ; data at  $25^\circ$ .

$n_0)/c$ , where *c* is the formal concentration of sodium *p*-toluenesulfonate; and *R*, computed from these quantities in the standard way.<sup>4</sup> The plot of *R* vs. wt. %  $\text{H}_2\text{SO}_4$  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

estimated recently as  $-0.6$  by a quite different method.<sup>12</sup>

- (5) K. Fajans, H. Kohner and W. Geffcken, *Z. Elektrochem.*, **34**, 1 (1928).
- (6) H. Kohner and M. L. Gressmann, *Z. physik. Chem.*, **A144**, 137 (1930).
- (7) W. Geffcken and A. Kruis, *ibid.*, **B23**, 175 (1933).
- (8) A. E. Brodskii, *Trans. Faraday Soc.*, **33**, 256 (1937).
- (9) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 269.
- (10) N. C. Deno, H. J. Peterson and E. Sacher, *J. Phys. Chem.*, **65**, 199 (1961).
- (11) G. C. Hood, O. Redlich and C. A. Reilly, *J. Chem. Phys.*, **22**, 2067 (1954).
- (12) K. N. Bascombe and R. P. Bell, *J. Chem. Soc.*, 1096 (1959).
- (13) Bell Telephone Laboratories, Inc., Murray Hill, New Jersey.

CHEMISTRY DEPARTMENT  
FLORIDA STATE UNIVERSITY  
TALLAHASSEE, FLORIDA

BENJAMIN J. BERKOWITZ  
ERNEST GRUNWALD<sup>13</sup>

**MOLECULAR GEOMETRY AND THE VAPOR PRESSURE OF ISOTOPIC MOLECULES. THE EQUIVALENT ISOMERS *cis*-, *gem*- AND *trans*-DIDEUTERIOETHYLENES<sup>1</sup>**

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  $130$ – $180^\circ\text{K}$ . 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.

- (1) A. Hantzsch, *Z. physik. Chem.*, **65**, 41 (1908).
- (2) K. Fajans and G. Joos, *Z. Physik*, **23**, 1 (1924).
- (3) K. Fajans, *Z. physik. Chem.*, **B24**, 103 (1934).
- (4) N. Bauer, in "Physical Methods of Organic Chemistry," A. Weissberger, ed., Interscience Publishers, Inc., New York, N. Y., 2nd ed., 1949, p. 1160.