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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RECEIVED AUGUST 2, 1948

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

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

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

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

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

(A)

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

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

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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RECEIVED AUGUST 20, 1948

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.$^{-1}$
ϵ_{max}	230	1,080
f	0.004	0.021
$^1A_{1g}$–$^1B_{1u}$ type forbidden transition		
Onset	46,300	near 47,500
ϵ_{max}	8,100	7,000
f	0.12	0.12
$^1A_{1g}$–$^1E_{1u}$ type allowed transition		
Peak	53,000	56,100
ϵ_{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-

(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.

(1) Kindly supplied by Dr. E. T. McBee.

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

tion spectra to the remarkably short limit of 1565 Å. using *n*-perfluoroöctane as a solvent.[3]

The fluoro spectrum is peculiarly free of any visible vibrational structure. The 3100 cm.$^{-1}$ blue shift of the $N \rightarrow V$ transition on complete fluorination is to be compared with a blue shift of 500 cm.$^{-1}$ in para-fluorotoluene with respect to toluene itself. This seems to indicate a shift of about 500 cm.$^{-1}$ per F. Spectra being determined on di- and tri-fluoro derivatives will indicate whether this result holds for the intermediate cases. These blue shifts are probably related to the high ionization potential of atomic fluorine, higher than that of any other combining element, and may represent increased ionization potential of the ring system with increased fluorine substitution.

Further detailed analyses of these and other fluorine-substituted benzenes are under way. It is hoped that a tetrafluoro- and a hexafluorobenzene will soon become available.

(3) H. B. Klevens and J. R. Platt, *J. Chem. Phys.*, **16**, Nov. (1948).

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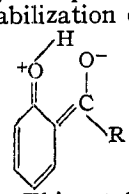
RECEIVED SEPTEMBER 1, 1948

MOLAR REFRACTION AND HYDROGEN BONDING

Sir:

The exaltations, 0.6 and 0.8 ml., observed in the molar refractions (D line) of salicylaldehyde and *o*-hydroxyacetophenone have been attributed[1] to the stabilization of the highly polar resonance structure  by intramolecular hydrogen bonding. This stabilization increases the mobility of the π electrons and thereby increases the polarizability of the molecules.

It occurred to the authors that similar exaltations should be observed in hydrogen bonding solvents for compounds having electron releasing and electron attracting groups at the ends of conjugated chains. The highly polar structure $R_2N^+{=}C_6H_4{=}CHO^-$ contributing to *p*-dimethylaminobenzaldehyde, for example, should be stabilized preferentially by solvent molecules having positive hydrogen atoms. These exaltations have been observed. The molar refraction obtained for this compound in benzene, 51.4 ml., is increased by 1.7 ml. in chloroform and 2.9 ml. in alcohol. Somewhat smaller exaltations have been observed in chloroform and alcohol for anisaldehyde and *p*-nitroanisole.

It was anticipated that the highly polar structure $H_2N^+{=}C_6H_4{=}C(CH_3){-}O^-$ contributing to *p*-aminoacetophenone would be stabilized in alcohol to a greater extent than in dioxane, as the former solvent can form hydrogen bonds with both the amino hydrogens and the carbonyl oxygen. The molar refraction of this compound was observed to increase from 44.3 in dioxane to 45.87 in ethyl alcohol. A similar increase was observed for *p*-nitroaniline.

The molar refraction of diethyl ketone in benzene, 25.12, increases only to 25.22 and 25.21 in chloroform and ethyl alcohol, indicating that hydrogen bonding does not result in any significant increase in polarizability for molecules that are not stabilized by the contribution of highly polar resonance structures.

This research is being continued to study the relative effects of various terminal groups, of double and triple bonds in the conjugated chain, and of mixed solvents on this exaltation.

(1) Curran, THIS JOURNAL, **67**, 1835 (1945).

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RECEIVED SEPTEMBER 15, 1948

THE ISOLATION OF A SUBSTANCE WITH Rh HAPTEN ACTIVITY

Sir:

It has been reported by Carter[1] that ether extraction of Rh-positive red blood cells produced a crude extract containing Rh hapten. We have been able to isolate from such extracts of pooled (A, B, AB and O) Rh-positive human cells a crystalline compound, m. p. 156.9–157.2°, having activity in dilutions of 1:5000 as measured by complement-fixation with anti-Rh_0 serum.[1c,2]

Crude extract[3] prepared according to Mrs. Carter's directions[1a] was freed of phospholipids (*ca.* 25–50% of the material) by precipitation from ether with acetone and the soluble portion was chromatographed from pentane saturated with 95% methanol on silica gel impregnated with the same solvent. A number of fractions containing crude cholesterol were obtained followed by fractions which yielded glistening needles by recrystallization from ether–pentane or chloroform–pentane solution, m. p. 156.9–157.2°. From 979 mg. of crude extract, 80 mg. of the pure hapten was obtained.

(1) (a) Carter, *Am. J. Clinical Path.*, **17**, 646 (1947); (b) Carter, *Am. J. Obst. and Gynecology*, **55**, 1051 (1948); (c) Carter, *J. Immunology*, in press.

(2) We are very grateful to Mrs. Bettina Carter, of the Institute of Pathology, Western Pennsylvania Hospital, Pittsburgh, Pa., for carrying out the assay of Rh activity by complement fixation according to Kolmer and Boerner, "Approved Laboratory Techniques," 4th ed., D. Appleton–Century, New York, N. Y., 1945, p. 674).

(3) We are indebted to Dr. E. D. Campbell and H. J. Henry of Eli Lilly and Company for several samples of crude extract and to Dr. C. S. Culbertson, South Bend Medical Foundation, and Dr. S. O. Levinson, Michael Reese Research Foundation, Chicago, for samples of blood cells.