$K = 0.841, 0.832, 0.825, 0.837$ 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.

ARGONNE NATIONAL LAB.
CHICAGO 80, ILL. HAROLD M. FEDER

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 dichlorooöctane (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

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

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

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

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

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

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

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.

GEORGE HERBERT JONES LABORATORY
THE UNIVERSITY OF CHICAGO M. S. KHARASCH
CHICAGO 37, ILLINOIS A. F. ZAVIST

RECEIVED AUGUST 20, 1948

---

[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.$^{-1}$
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] Kindly supplied by Dr. E. T. McBee.

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