afforded 6.70 g. (89%) of ethyl benzoate, b.p. 95–96° (15 mm.), n^{20}_{D} 1.5048; reported b.p. 87° (10 mm.),[11] n^{20}_{D} 1.5057.[12] A second fraction consisted of 7.40 g. (90%) of ethyl *p*-toluate, b.p. 107° (11 mm.), n^{20}_{D} 1.5082; reported b.p. 110°(12 mm.),[13] n^{18}_{D} 1.5089.[13] Acenaphthene was used as a "chaser."

Reaction of Hydrazoic Acid with *p*-Methylbenzophenone. A.—To a mixture of 51.5 cc. (0.92 mole) of concentrated sulfuric acid, 19.6 g. (0.1 mole) of *p*-methylbenzophenone and 200 cc. of benzene was added 7.8 g. (0.12 mole) of sodium azide, in small portions, during two hours, at room temperature. The mixture was then warmed to 45–55° until the theoretical volume of nitrogen had evolved (8 hours). The reaction mixture was poured on crushed ice, partially neutralized with 10% sodium hydroxide solution, then made basic with saturated sodium carbonate solution. The mixture was extracted with ether, and the ether solution washed with dilute hydrochloric acid and 10% sodium carbonate solution. The ether solution was dried over anhydrous magnesium sulfate, filtered and the ether evaporated. There remained 18.7 g. of solid material, which was hydrolyzed by refluxing for five days with a mixture of 400 cc. of glacial acetic acid and 100 cc. of 40% hydrobromic acid. The mixture was diluted and extracted with ether. The ether solution was washed with water, dried over anhydrous sodium sulfate, filtered and the ether evaporated. There remained 12.8 g. of mixed solids containing benzoic and *p*-toluic acids.

The acids were esterified and fractionated as described above for the known mixture. There was obtained 4.00 g. (31%) of ethyl benzoate, b.p. 96–97° (17 mm.), n^{20}_{D} 1.5066 and 4.25 g. (33%) of ethyl *p*-toluate, b.p. 115–116° (17 mm.), n^{20}_{D} 1.5090.

B.—The procedure of Sherk, *et al.*,[2] was employed on 19.6 g. (0.1 mole) of *p*-methylbenzophenone. The reaction mixture was handled as in A. There was obtained 6.2 g. (41.3%) of ethyl benzoate, b.p. 96–98° (18 mm.), n^{20}_{D} 1.5048 and 6.0 g. (36.6%) of ethyl *p*-toluate, b.p. 118–119° (19 mm.), n^{20}_{D} 1.5083.

Schmidt Reaction of *p*-Methoxybenzophenone.—*p*-Methoxybenzophenone, 22.7 g. (0.1 mole), was reacted in the same manner as that described for *p*-methylbenzophenone, part A, except that the temperature was maintained at 25–30° throughout the reaction, and a benzene solution of hydrazoic acid was used instead of sodium azide. There was a large amount of tar formed, which was ether insoluble. From the ether solution there was obtained 18.7 g. of mixed neutral solids. On digestion with a small amount of ether, 8.0 g. of *p*-methoxybenzophenone was recovered from the ether solution. The remaining 10.7 g. of neutral solids was refluxed for five days in a solution of 90 g. of potassium hydroxide in 500 cc. of ethanol. The ethanol was distilled *in vacuo*, the residual solid dissolved in water and extracted with ether. Addition of hydrochloric acid to the aqueous layer precipitated the carboxylic acids, which were taken up in ether and dried over anhydrous sodium sulfate. Evaporation of the ether afforded 3.3 g. of mixed acids.

Anal. Found: methoxyl, 6.83, 7.04.

The analytical results indicate the presence of about 34% of *p*-anisic acid and 66% of benzoic acid.

1-α-Pyridyl-2-azidoethane.—Under the same conditions as employed in the Schmidt reaction of unsymmetrical diarylethylenes,[6] there was obtained a 17% yield of 1-α-pyridyl-2-azidoethane, b.p. 91° (8.5 mm.), 84–85° (4.5 mm.), 58° (0.6 mm.). The same substance was obtained in 97% yield by use of Boyer's procedure.[9]

Mercuric Chloride Addition Product.—Crystallized from 95% ethanol, the colorless addition product melted at 117°.

Anal. Calcd. for $C_7H_8N_4HgCl_2$: C, 20.13; H, 1.45; N, 13.41. Found: C, 19.91, 19.64; H, 1.60, 1.75; N, 13.14.

Catalytic Reduction of 1-α-Pyridyl-2-azidoethane.—A solution of 8.90 g. (0.06 mole) of 1-α-pyridyl-2-azidoethane in 30 cc. of absolute ethanol was hydrogenated at three atmospheres in a Parr apparatus for 24 hours over 0.10 g. of platinum oxide catalyst. The solution smelled of ammonia. Distillation afforded 3.1 g. (35%) of β-2-pyridylethylamine, b.p. 76–78° (4 mm.), reported[14] b.p. 92–93° (12 mm.).

Picrate.—Yellow needles were obtained from ethanol, m.p. 213–215°; reported[14] 215–216°.

Dihydrochloride.—Colorless crystals were obtained, m.p. 186–189°; reported m.p. 185–186°,[15] 189°.[16]

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Molecular Refractions of the SO_3 and SO_2Cl Groups in *p*-Ethylbenzenesulfonyl Chloride and the Methyl, Ethyl and *n*-Butyl Esters of *p*-Ethylbenzenesulfonic Acid

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During a study of *p*-ethylbenzenesulfonyl chloride and its derivatives we have prepared three new esters derived from the sulfonyl chloride and obtained previously unrecorded constants for the compounds. The density and refractive index data gave molecular refraction values for the SO_3 and SO_2Cl groups showing deviations from the rather narrow range of values previously recorded for these groups in other compounds. We wish to record at this time the results of these observations.

p-Ethylbenzenesulfonyl chloride was prepared by the action of phosphorus pentachloride on the crude sulfonic acid.[2] The sulfonic acid was prepared by reaction of excess ethylbenzene with concd. sulfuric acid under conditions which permitted removal of the water formed during the reaction as the ethylbenzene–water azeotrope. The reaction was continued until the theoretical amount of water was collected. The sulfonyl chloride was obtained in 47% yield based on the amount of sulfuric acid used. It was characterized as the previously described[2b,2d,3] amide, m.p. 108°.

The fact that the amide prepared from this sulfonyl chloride consists chiefly of the isomer which melts at 108° is considered good evidence that the material is substantially pure *p*-ethylbenzenesulfonyl chloride. Also, it is known that mixtures of ortho and para isomers are obtained from low temperature (0°) sulfonations[3b] and that the ortho isomer rearranges to the para isomer at 100°.[2d] The pure amide of the ortho isomer melts at 126°.[3b] The sulfonation was run at 115° in our experiments. The crude amide, m.p. 97–106°, was obtained in 95% yield from the sulfonyl chloride.

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[1] This work was supported in part under Contract No. AT-(40-1)-229 between the Atomic Energy Commission and the University of Louisville. Taken from a thesis submitted by R. P. D. in partial fulfillment of the requirements for the M.S. degree.

[2] (a) P. Chruschtschow, *Ber.*, **7**, 1164 (1874); (b) L. Semptowski, *ibid.*, **22**, 2673 (1889); (c) A. Tohl and O. Eberhard, *ibid.*, **26**, 2940 (1893); (d) G. T. Moody, *ibid.*, **29R**, 663 (1896).

[3] (a) J. Moschner, *ibid.*, **34**, 1257 (1901); (b) R. Fricke and G. Spilker, *ibid.*, **58**, 1589 (1925).

The total yield of recrystallized amide m.p. 108° from the crude amide is 4.2 g. or 89% of the theoretical. No evidence of the amide of the ortho isomer reported[3b] to melt at 126° and to have a different crystalline form was observed.

The methyl, ethyl and *n*-butyl esters of *p*-ethylbenzenesulfonic acid were prepared in 61–71% yields by reactions of the sulfonyl chloride with the alcohol in the presence of sodium hydroxide[4] or pyridine[5] using previously described techniques.

Attempts were made to prepare other esters from the sulfonyl chloride and the following alcohols: isopropyl, *n*-amyl, *s*-butyl, benzyl and 2-ethylhexyl. In all cases liquids were obtained which did not solidify at low temperatures and decomposed on attempted distillation presumably to give olefins and the sulfonic acid. The latter was isolated and identified as a product of the decomposition of the amyl ester. These data suggest that the *p*-ethylbenzenesulfonates decompose more readily on heating and melt lower than the corresponding *p*-toluenesulfonates.

Molecular refraction data obtained from our density and refractive index measurements gave values of 9.95 to 10.72 for the SO_3 group in the *p*-ethylbenzenesulfonates and 16.77 for the SO_2Cl group in *p*-ethylbenzenesulfonyl chloride. Preliminary comparison of these values with those previously reported in the literature indicated rather wide deviations. For comparison, values from several sources are given in Table I along with our data for the *p*-ethylbenzene derivatives, some previously unrecorded data for *p*-toluenesulfonates, and our redetermination of the value for benzenesulfonyl chloride. In these calculations the values for the group increments given by Eisenlohr[6a] were used.

TABLE I

MOLECULAR REFRACTIVITY DATA

Compound	Sp. gr.[a]	n_D[a]	M_D (obsd.)	Group increments[b]
Benzenesulfonyl chloride	1.378 (23°)[c]	1.5505 (23°)[c]	40.93	15.72[c,d]
	1.3778 (23°)	1.5507 (23°)	40.94	15.73[d]
p-Ethylbenzenesulfonyl chloride	1.268	1.5469 (20°)	51.22	16.77[d]
Alkane and alkenesulfonyl chlorides	...	....	...	15.33–15.52[c,d]
Methyl PEBS[e]	1.193	1.5181 (20°)	50.88	10.72[f]
Ethyl PEBS[e]	1.178	1.5150 (20°)	54.73	9.95[f]
n-Butyl PEBS[e]	1.114	1.5051 (20°)	64.53	10.54[f]
n-Propyl PTS[e]	1.144	1.4998	55.00	10.12[f]
n-Butyl PTS[e]	1.120	1.5050	60.38	10.99[f]
n-Amyl PTS[e]	1.100	1.5028	65.02	11.01[f]
Allyl PTS[e]	1.175	1.5242	56.51	12.20[f]
Alkyl ethylenesulfonate[g]	...	....	...	8.99–9.83[f]

[a] Data obtained in the present studies except as otherwise indicated; sp. gr. at 20°/20° and n_D at 20° except as noted. [b] Based on Eisenlohr constants given in reference 6a. [c] From reference 8. Revised using Eisenlohr constants. [d] For SO_2Cl group. [e] PEBS = *p*-ethylbenzenesulfonate; PTS = *p*-toluenesulfonate. [f] For SO_3 group. [g] From reference 9. Revised using Eisenlohr constants.

The value for the SO_3 group, obtained as the difference between the observed molecular refraction and the sum of the group refractions including double bond exaltations, varies from 8.99 to 12.20. The value varies from 9.95–10.72 in three *p*-ethylbenzenesulfonates; from 10.12 to 12.20 in four *p*-toluenesulfonates; and from 8.99 to 9.83 in seven alkyl[7] ethylenesulfonates. The values for the *p*-toluenesulfonates not previously reported were obtained from density and refractive index values given previously.[7] The highest value of 12.20 is obtained from the data for allyl *p*-toluenesulfonate. Allyl structures are known to cause anomalies[6b] and if this value is omitted, as has been done in previous studies, the variation is from 9.95 to 11.01.

The value for the SO_2Cl group, also obtained by difference, varies from 15.31 to 16.77. Much less information is available for evaluation of the variation in the increment for this group. In four alkane and alkene sulfonyl chlorides the value varies from 15.33 to 15.52[8]; our value for *p*-ethylbenzenesulfonyl chloride is 16.77 and the previously reported[8] value for benzenesulfonyl chloride is 15.73. Our redetermination of the density and refractive index for the latter was in good agreement with previously recorded values and gives the same value for the SO_2Cl group increment.

The variations in values for these two groups—SO_3 and SO_2Cl—appear to fall within recognized limits. Variations of this order have been observed in the increments for other groups. Examples are the variations from 0.68 to 1.60 for fluorine and from 1.53 to 1.94 for the carbon–carbon double bond. The significance of such variations has been discussed previously.[6b] It is apparent, however, that the variations in the values for SO_3 and SO_2Cl are considerably greater than has been indicated in previous evaluations[8–10] of the values for these increments.

The ultraviolet absorption curves for the *p*-ethylbenzenesulfonic acid esters and chloride all show an absorption maximum at 264 ± 2 mμ. This appears to be the 255 mμ peak usually associated with the benzene nucleus shifted to slightly longer wave lengths by the sulfonate or sulfonyl chloride group. The four curves are similar and do not indicate the individuality of the chloride observed in the molecular refraction data.

Experimental[11]

***p*-Ethylbenzenesulfonyl Chloride.**—Ethylbenzene was sulfonated with concentrated sulfuric acid at reflux in a continuous process. The crude acid was converted to the sulfonyl chloride by reaction with phosphorus pentachloride. Refractionation through a column packed with helices gave a fraction, b.p. 143° at 16 mm., n^{20}_D 1.5469, sp. gr. 20/20 1.268.

Reaction of the sulfonyl chloride with cold concd. ammonium hydroxide gave a precipitate of crystals. The dried crude product, m.p. 97–106°, weighed 4.5 g., 95% of the theoretical. One recrystallization from aqueous alcohol gave 3.3 g., 69.7% of the theoretical amount, of *p*-ethylbenzenesulfonamide, m.p. 108°. The total yield of pure amide, m.p. 108°, obtained by recrystallization of the crude amide was 4.2 g., 89% of the theoretical.

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[11] Sulfur analyses by Micro Tech Laboratories, Skokie, Illinois.

Methyl *p*-Ethylbenzenesulfonate.—A solution of 53 g. of *p*-ethylbenzenesulfonyl chloride in 63.5 ml. of methanol was placed in a reaction flask and cooled to 20° by immersion of the flask in a salt–ice-bath. The solution was stirred continuously while a solution of 40 g. of sodium hydroxide in 30 ml. of water was added slowly. The temperature was held at 23–25° during the addition. The reaction mixture was cooled to 0° and let stand for two hours. Sufficient water was added to dissolve the precipitated sodium chloride. The ester layer was decanted, washed with two 20-ml. portions of water and then with 40 ml. of a 5% sodium carbonate solution, dried over anhydrous sodium sulfate, and distilled to give 31.4 g. or 61% of the theoretical amount of methyl *p*-ethylbenzenesulfonate, b.p. 125–135° at 2 mm. Refractionation through a column packed with helices gave a sample, b.p. 128° at 2 mm., $n^{20}D$ 1.5181, sp. gr. 20/20 1.193, which was used for analysis.

Anal. Calcd. for $C_9H_{12}O_3S$: S, 16.0. Found: S, 15.85.

Ethyl *p*-Ethylbenzenesulfonate.—This ester was prepared using the procedure described for the methyl ester except that the reaction was run at 10°. The yield of ester b.p. 120–137° at 2 mm. was 20.9 g. or 67% of the theoretical amount. Refractionation through a column packed with helices gave a sample b.p. 142–150° at 4 mm., $n^{20}D$ 1.5150, sp. gr. 20/20 1.178, which was used for analysis.

Anal. Calcd. for $C_{10}H_{14}O_3S$: S, 14.95. Found: S, 14.70.

***n*-Butyl *p*-Ethylbenzenesulfonate.**—A mixture of 30 g. of *p*-ethylbenzenesulfonyl chloride and 18 ml. of *n*-butanol was cooled to 5°. To this solution, 23 ml. of pyridine was added over a three-hour period while maintaining the reaction mixture at a temperature of 8–18°. The reaction mixture was cooled to 3° and treated with sufficient dil. hydrochloric acid to neutralize the pyridine. The ester layer was separated and taken up in ether. The ether solution was washed with water and with 5% sodium carbonate and dried over anhydrous sodium sulfate. On fractionation 25.3 g. or 71.6% of the theoretical amount of *n*-butyl *p*-ethylbenzenesulfonate, b.p. 148–150° at 2 mm., was obtained. Refractionation through a column packed with helices gave a sample, b.p. 159° at 4 mm., $n^{20}D$ 1.5051; sp. gr. 20/20 1.114.

Anal. Calcd. for $C_{12}H_{18}O_3S$: S, 13.22. Found: S, 13.38.

Ultraviolet Absorption Data.—Ultraviolet absorption measurements were made with a Beckman DU photoelectric spectrophotometer using 1.00-cm. silica cells and hydrogen and tungsten discharge lamps as light sources. In all measurements 95% ethanol was used as a solvent. The esters and chloride showed an absorption maximum at 264 ± 2 mμ.

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The Charge Transfer Reaction between Molybdo- and Molybdioctacyanides[1]

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The high coördination number and the apparently very close structural similarity of the octacyanides of Mo(IV) and Mo(V) as well as, to a lesser extent, their high net charges lends interest to the charge transfer process between these two complexes. In particular, this case should be a significant indication of the validity of Libby's proposal[2] that the Franck–Condon principle is of primary importance in determining the rates of oxidation–reduction reactions in solution.

$K_4Mo(CN)_8$ and $K_3Mo(CN)_8$ were prepared by the method described by Willard and Thielke.[3] The same compounds containing 66-hr. Mo^{99} were made from MoO_3 irradiated in the Brookhaven reactor. The purity of the $K_4Mo(CN)_8$ was found by titration with $KMnO_4$ to be 99.9%. Decomposition of $K_3Mo(CN)_8$ to $K_4Mo(CN)_8$—a photo-induced reaction—was found to be negligible in the time of the runs.

Three different separations of the two complexes were developed: (1) Several organic solvents miscible with water were found to precipitate $Mo(CN)_8^{-4}$ while leaving $Mo(CN)_8^{-3}$ in solution. This method is effective at concentrations greater than $\sim 10^{-3} f$. In practice separations were carried out by adding five volumes of absolute alcohol to one volume of reactant solution. (2) Cd(II) gives good precipitates with $Mo(CN)_8^{-4}$ at concentrations down to $\sim 10^{-3} f$ while leaving $Mo(CN)_8^{-3}$ in solution. (3) Tetraphenylarsonium chloride was found to give filterable precipitates with concentrations of $Mo(CN)_8^{-3}$ down to 10^{-4}–10^{-5} f. In basic solution $Mo(CN)_8^{-4}$ gave no precipitate, while in acid solution the concentration of $Mo(CN)_8^{-4}$ had to be kept below $\sim 10^{-3} f$ to prevent precipitation.

After separation by one of the above techniques, the second species was precipitated by a suitable method. Following a one-day wait to allow equilibration of the daughter Tc^{99m} both fractions were counted.

Using the above techniques over a wide range of *p*H and of anions present in solution, all experiments showed complete exchange, within the experimental error of 10%, in the approximately 5 seconds required for separation. Table I gives the conditions under which some typical experiments were carried out. All runs were made in very dim light at a temperature of 2 ± 1°.

The exchange between one of the species freshly precipitated by the separating agent and the other species was also measured in a series of runs analogous to those in Table I. In all cases a definite but incomplete heterogeneous exchange was found.

The possibility exists that in the homogeneous reaction the complete exchange found is induced by the separation.[4] The likelihood of this is decreased by the use of three distinct separation methods (although in this connection it would have been advantageous if a rapid non-precipitation technique could also have been used). It may be concluded that the charge exchange between $Mo(CN)_8^{-3}$ and $Mo(CN)_8^{-4}$ in aqueous solution is probably an extremely rapid process with a rate constant, if a second-order rate law is obeyed, greater than 10^3 f^{-1} sec.$^{-1}$ at 2°.

It has been shown that the cyanides attached to the central Mo do not exchange.[5] This fact in conjunction with the high degree of coördination involved makes it very unlikely that this charge transfer reaction proceeds by a radical or ion-exchange mechanism. It seems probable then that a true homogeneous electron transfer process is involved here.

Magnetic susceptibility measurements show that $K_4Mo(CN)_8$ is diamagnetic while $K_3Mo(CN)_8$ has a paramagnetism corresponding to one unpaired

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

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