up and a white precipitate formed. When addition was complete, the green mixture was poured onto ice and the product was collected and washed with water. The product was soluble in 10% sodium hydroxide and in 10% sodium bicarbonate. Recrystallization from acetone–water yielded 0.145 g. (51%) of colorless III, m.p. 301–305° dec. (uncor.); infrared spectrum: C=O, 5.72(s), 5.92(s); C=C, 6.20(s) μ.

Anal. Calcd. for $C_{10}H_4Cl_2O_4$: C, 46.4; H, 1.6; Cl, 27.4. Found: C, 46.7; H, 1.6; Cl, 27.1.

COLUMBUS 10, OHIO

COMMUNICATIONS TO THE EDITOR

THE FUOSS–ONSAGER CONDUCTANCE EQUATION AT HIGH CONCENTRATIONS

Sir:

Fuoss and Onsager,[1,2] in presenting their theory of the conductance of free ions, were careful to point out that it is applicable to dilute solutions below a concentration where the value of κa is less than 0.2. They have demonstrated the validity of the theory below this concentration but, at this writing, the behavior of their conductance equation has not been investigated at higher concentrations. Mercier and Kraus[3] have measured the conductance of dilute solutions of tetramethylammonium picrate up to about 3×10^{-3} *N* in dioxane–water mixtures from pure water up to 70% dioxane. An analysis by Fuoss and Kraus[4] indicates that this electrolyte is completely dissociated over this entire range of mixtures. Accascina, prior to the advent of the Fuoss–Onsager theory, measured the conductance of Me_4NPi in a 55% dioxane–water mixture to a concentration of 0.226 *N*. Subsequently, Kay analyzed the data using an IBM computer[5] and obtained 33.39 and 6.14 $\times 10^{-8}$ for Λ_0 and a, respectively. The results are shown graphically in Fig. 1.

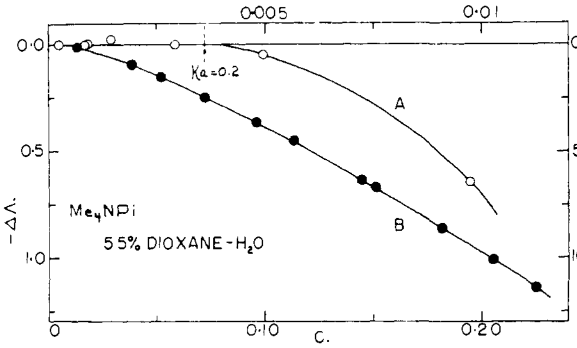

Fig. 1.—Deviation between observed and calculated equivalent conductances· A, dilute range, coördinates left and above; B, entire range, coördinates right and below.

In plot A of this figure are shown values of $\Delta\Lambda = \Lambda_{obs} - \Lambda_{calc}$ plotted as functions of *C* for concentrations up to 0.01 *N*. It will be noted that the calculated values of Λ closely approximate those observed at concentrations below 3×10^{-3} *N*. The average deviation between the terms is 0.015 Λ-unit or 0.05%. At concentrations above 4×10^{-3} *N*, calculated values begin to diverge from the experimental ones. The concentration at which $\kappa a = 0.2$ is 3.6×10^{-3} *N*. Thus, deviations are within experimental error below this concentration but increase markedly at concentrations much beyond this limit. Plot B of Fig. 1 covers the entire concentration range up to 0.226 *N*. It can be seen that up to about 0.01 *N* the differences are not large enough to show on the plot. At higher concentrations, the difference increases, reaching very large values at high concentration. At the highest concentration, the calculated conductance is almost seven times the measured value.

The results of this analysis show rather convincingly that the theory reproduces the experimental values closely over the concentration range in which the approximations made in deriving the theory are justified, but, as expected, at higher concentrations the deviations become steadily greater than the experimental error. The experimental data will be presented elsewhere in due course.

UNIVERSITÀ DEGLI STUDI DI ROMA
ISTITUTO DI CHEMICA-FISCA
ROME, ITALY, AND FILIPPO ACCASCINA
METCALF RESEARCH LABORATORY
BROWN UNIVERSITY ROBERT L. KAY
PROVIDENCE, R. I. CHARLES A. KRAUS

RECEIVED MARCH 9, 1959

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(1) R. M. Fuoss and L. Onsager, *J. Phys. Chem.*, **61**, 668 (1957).

(2) R. M. Fuoss, THIS JOURNAL, **80**, 3163 (1958).

(3) P. L. Mercier and C. A. Kraus, *Proc. Nat. Acad. Sci.*, **41**, 1033 (1955).

(4) R. M. Fuoss and C. A. Kraus, THIS JOURNAL, **79**, 3304 (1957).

(5) Program No. 004 at the Brown Computing Center

RELATIVE ARYL RADICAL AFFINITIES OF MONOMERS

Sir:

Evidence[1,2,3] has been presented that the mechanism of the Meerwein reaction involves addition of an aryl radical to a monomer followed by rapid halogen transfer from cupric chloride or from a higher chloro-complex. Thus, competitive Meerwein reactions might provide the means for measuring relative rate constants for the addition of aryl radicals to olefins. This possibility has now been realized.

Acrylonitrile (A) and methacrylonitrile (MA) were selected as reference monomers. In a typical experiment 0.4 mole of both methyl acrylate and acrylonitrile were allowed to compete for the phenyl

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(1) S. C. Dickerman, K. Weiss and A. K. Ingberman, *J. Org. Chem.*, **21**, 380 (1956); THIS JOURNAL, **80**, 1904 (1958).

(2) S. C. Dickerman and K. Weiss, *J. Org. Chem.*, **22**, 1070 (1957).

(3) J. K. Kochi, THIS JOURNAL, **79**, 2942 (1957).

radicals generated from 0.02 mole of diazonium salt. The reaction was carried out at 25° under nitrogen in an aqueous-acetone solution of cuprous and cupric chlorides. Polymerization appeared to be completely inhibited.[1,3] The mixture of Meerwein-type products was analyzed by a modified Kjeldahl method[4] and by a procedure which measures aliphatic-bound halogen.[5] The molar ratio of products is expressed in Table I as a ratio of rate constants, k_M/k_A.[6] Results with other monomers are given in the first column of Table I. Phenyl affinities of these olefins also were measured relative to methacrylonitrile and are reported in the second column of Table I. Use of two reference nitriles permits several calculations of the phenyl affinity of methacrylonitrile relative to that of acrylonitrile, k_{MA}/k_A in Table I, and the constancy of this value demonstrates the internal consistency of our findings. Furthermore, the relative reactivities are insensitive to changes in concentration of both cuprous and cupric chlorides. Table II presents similar data obtained for the *p*-chlorophenyl radical.

TABLE I

RELATIVE PHENYL AFFINITIES

Monomer (M)	k_M/k_A	k_M/k_{MA}	k_{MA}/k_A (calcd.)
Methyl acrylate	0.79 ± 0.03[a]	0.69 ± 0.02	1.15 ± 0.07
Styrene	0.86 ± 0.02	0.74 ± 0.02	1.16 ± 0.04
Acrylonitrile (A)	1.00[b]	. . .	. . .
Methyl methacrylate	1.07 ± 0.01	0.93 ± 0.06	1.15 ± 0.08
Methacrylonitrile (MA)	. . .	1.00[b]	. . .

[a] Average deviation of a single determination. [b] Reference monomer.

TABLE II

RELATIVE *p*-CHLOROPHENYL AFFINITIES

Monomer (M)	k_M/k_A
Methyl acrylate	0.97 ± 0.04[a]
Acrylonitrile (A)	1.00[b]
Styrene	1.47 ± 0.03
Methyl methacrylate	1.52 ± 0.06

[a] Average deviation of a single determination. [b] Reference monomer.

Since the results appear unique, correlation must be attempted with data obtained for radicals other than aryl. The methyl affinities[7] of styrene, acrylonitrile and methyl methacrylate have been determined and parallel the phenyl affinities of these monomers. Studies of copolymerization have evolved a well-known reactivity sequence[8] which has been partially corroborated by investigations with trichloromethyl and acyl radicals.[9] The *p*-chlorophenyl affinities of Table II are in agreement with this sequence. The different position of styrene in Tables I and II undoubtedly reflects the polar character of the *p*-chlorophenyl radical and suggests that a part of the "standard" sequence[8] should be restricted to reactions which involve electrophilic or acceptor radicals.

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(4) S. Rovira, *Ann. chim.*, **20**, 660 (1945).

(5) J. K. Kochi, THIS JOURNAL, **78**, 1228 (1956).

(6) This type of competitive experiment has been used extensively by Hey and others in studies of homolytic aromatic substitution. For a discussion of the assumptions involved and original references see D. R. Augood, D. H. Hey and G. H. Williams, *J. Chem. Soc.*, 2094 (1952).

(7) F. Leavitt, M. Levy, M. Szwarc and V. Stannett, THIS JOURNAL, **77**, 5493 (1955); M. Szwarc, *J. Polymer Sci.*, **16**, 367 (1955).

(8) Styrene > acrylonitrile > methyl acrylate. For recent discussion and references, see C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y.

(9) R. L. Huang, *J. Chem. Soc.*, 1749 (1956); 1342 (1957).

WM. H. NICHOLS CHEMICAL LAB. S. C. DICKERMAN
NEW YORK UNIVERSITY I. S. MEGNA
NEW YORK 53, N. Y. M. M. SKOULTCHI

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X-RAY DETERMINATION OF THE STRUCTURE OF TRICARBONYLCHROMIUM-BENZENE

Sir:

In connection with the studies carried out in our Institute by G. Natta, R. Ercoli and F. Calderazzo on the synthesis[1] and properties[2] of tricarbonylchromium-arenes, we have undertaken a detailed X-ray structural investigation of tricarbonylchromium-benzene, and we wish to communicate some preliminary results of our work.

Single crystals of tricarbonylchromium-benzene were examined by Weissenberg methods; we found $a = 6.58 \pm 0.04$ Å.; $b = 10.99 \pm 0.06$ Å.; $c = 6.09 \pm 0.04$ Å. and $\beta = 101°30'$; $N = 2$.

The choice of possible space groups, from the systematic absence of 0*k*0 reflections with *k* odd, is confined to $P2_1$ or $P2_1/m$.

The Patterson projections along the *a* and *c* axes gave a definite evidence of the existence of a symmetry plane through the chromium atoms.

Accordingly, we assumed that the space group is $P2_1/m$. The chromium fractional coördinates are: $x = 0.022, y = 0.250, z = 0.331$.

We have carried out Fourier projections of the electron density along the *a* and *c* axes; as an example, in Fig. 1 the projection of the electron

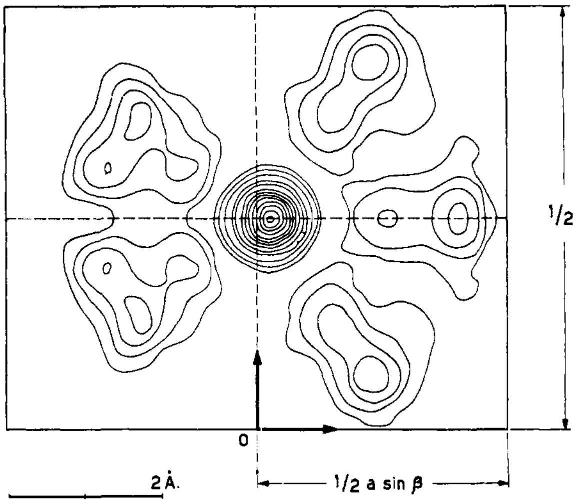

Fig. 1.—Fourier projection of the electron density along the *c* axis. The contours drawn are 2, 4, 6, 8, 10, 14, 18 . . . $e/Å.^2$

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(1) G. Natta, R. Ercoli and F. Calderazzo, *Chimica e Industria*, **40**, 287 (1958).

(2) G. Natta, R. Ercoli, F. Calderazzo and E. Santambrogio, *ibid.*, **40**, 1003 (1958).