

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 method⁴ 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 affinities⁷ 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 sequence⁸ which has been partially corroborated by investi-

(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.*, **18**, 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.

gations 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" sequence⁸ should be restricted to reactions which involve electrophilic or acceptor radicals.

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

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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 synthesis¹ and properties² 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 $a = 6.58 \pm 0.04 \text{ \AA}$; $b = 10.99 \pm 0.06 \text{ \AA}$; $c = 6.09 \pm 0.04 \text{ \AA}$ and $\beta = 101^\circ 30'$; $N = 2$.

The choice of possible space groups, from the systematic absence of $0k0$ 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 coordinates 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

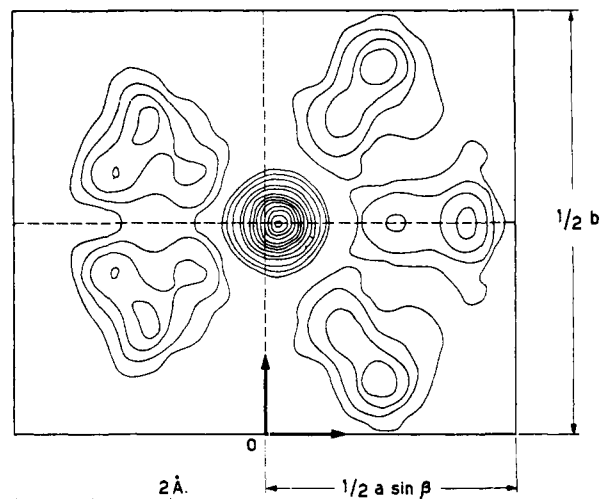


Fig. 1.—Fourier projection of the electron density along the c axis. The contours drawn are 2, 4, 6, 8, 10, 14, 18 . . . $e/\text{\AA}^2$.

(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).

density along the c axis is given, in which carbon and oxygen atoms are fairly well resolved.

At this stage of the research, from the positions of the electron density maxima, we could deduce that: (1) the benzene carbon atoms have fixed positions and are all placed at the same distance (2.25 ± 0.05 Å.) from the chromium atom. (2) The plane in which the oxygen atoms are contained is parallel within experimental errors to the benzene ring. (3) The C and O atoms of each C=O group are collinear with the chromium atom. (4) The angles OC-Cr-CO are equal and very near to 90° (exp. 89°). The O-Cr distances are 2.95 ± 0.05 Å. (to compare with the value 3.08 Å. quoted for chromium hexacarbonyl).³

It seems to us that the model of the molecule thus established (see Fig. 2) favors the hypothesis

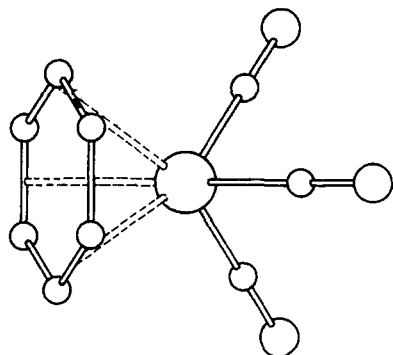


Fig. 2.—Model of the molecule corresponding to the Fourier projection of Fig. 1.

of a d^2sp^3 hybridization of the chromium atom in tricarbonylchromium-arenes.⁴

We acknowledge the helpful suggestions of Prof. G. Natta and Prof. R. Ercoli, who also supplied us the sample.

(3) L. O. Brockway, R. V. G. Ewens and M. W. Lister, *Trans. Faraday Soc.*, **34**, 1350 (1938).

(4) E. O. Fischer, K. Öfele, H. Essler, W. Fröhlich, J. P. Mortensen and W. Semmlinger, *Chem. Ber.*, **91**, 2763 (1958).

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COUNTERCURRENT DISTRIBUTION STUDIES WITH ADULT HUMAN HEMOGLOBIN

Sir:

A few experiments with hemoglobin have been made as part of a general study of the application of countercurrent distribution to proteins and peptides. In view of the ease with which the heme is dissociated from the protein, the latter was first studied and found to be resolved into more than one component.

Globin (about 150 mg.) prepared from carbonmonoxyhemoglobin¹ gave the distribution pattern of Fig. 1 in 2-butanol-1% aqueous dichloroacetic acid (1:1) at 82 transfers. Plots of partition ratios across the bands and experimental curves wider than the calculated indicated neither band to be entirely homogeneous at this stage.

(1) M. L. Anson and A. E. Mirsky, *J. Gen. Physiol.*, **13**, 469 (1930).

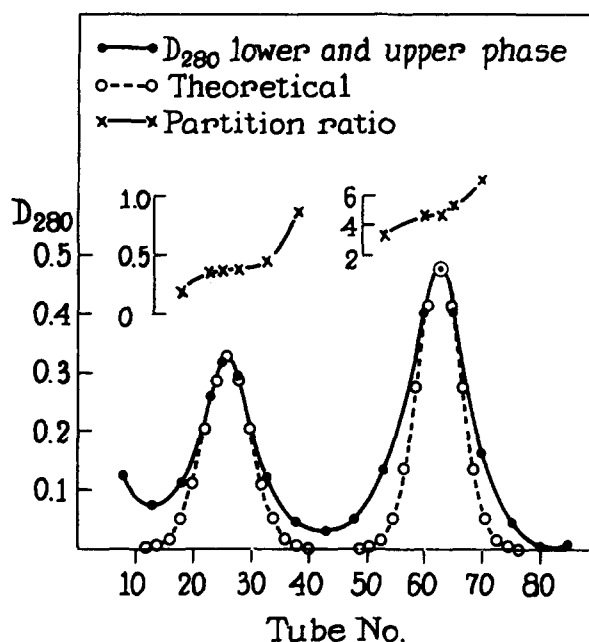


Fig. 1.—Countercurrent distribution pattern of the globin from hemoglobin.

Central cuts from each band were concentrated on a rotary evaporator to remove the butanol, then dialyzed against 0.1 *N* acetic acid and lyophilized.

A 30 mg. sample of each was converted to the dinitrophenyl derivative at pH 9 with 2,4-dinitrofluorobenzene (1 hr. at 40°). The recovered derivative was hydrolyzed in 6 *N* HCl for 15 min.² at 110° . The yellow ether-soluble material was distributed to 120 transfers in the system benzene-

TABLE I

AMINO ACID COMPOSITION OF 22-HOUR HYDROLYSATES OF α AND β COMPONENTS

Values are given as g. of amino acid per 100 g. protein (a correction of 13% bound DCA has been assumed).

Amino acid	α	β	Average α and β	Lit. ^{4,5} for normal white hemoglobin A
Aspartic	9.35	9.84	9.60	9.64
Threonine	5.78	4.61	5.20	5.13
Serine	6.03	2.82	4.43	4.05
Glutamic	4.42	8.77	6.60	6.55
Proline	4.83	4.82	4.83	5.02
Glycine	2.93	5.52	4.23	4.32
Alanine	10.60	7.37	8.99	9.15
Valine	8.37	12.22	10.30	10.36
Methionine	1.63	0.75 ^a	1.19	1.25
Leucine	13.35	14.62	13.99	13.94
Tyrosine	2.84	2.94	2.89	3.05
Phenylalanine	6.67	7.85	7.26	7.33
Lysine	9.75	9.50	9.63	9.28
Histidine	9.45	8.17	8.81	8.32
Arginine	3.20	3.38	3.29	2.82
Cysteine	0.74 ^a	1.32 ^a	1.03	0.73-1.10
Tryptophan ^b	1.27	2.48	1.88	2.03

^a Determined as cysteic acid or methionine sulfone after oxidation with performic acid. ^b Values calculated from absorption spectrum studies on intact protein.

(2) H. S. Rhinesmith, W. A. Schroeder and N. Martin, *This Journal*, **80**, 3358 (1958).