Fig. 1.—Variation of product ratios with concentration during chlorination of cyclohexene at 25.0°: $\bigcirc$, nitrogen in the dark; $\square$ nitrogen with illumination; $\triangle$, oxygen in the dark.

gen atom toward attack by chlorine atom; this ratio is 0.72 ± 0.02 over a 150-fold change in ratio of starting hydrocarbons.

TABLE I

DEPENDENCE OF PERCENTAGE OF RADICAL REACTION (r) ON CONCENTRATION IN CYCLOHEXENE CHLORINATION AT 25.0° IN THE ABSENCE OF LIGHT AND OXYGEN

Mole fraction cyclohexene[a]	r	$(I/II)_{calcd.}$	$(I/II)_{obsd.}$[b]
1.00	(100)		
0.50	97	2.01	1.95
.30	89	2.11	1.98
.20	79	2.26	2.11
.10	60	2.50	2.42
.050	41	2.72	2.71
.035	31	2.83	2.82
.020	20	2.94	2.95
.010	12	3.02	3.07

[a] Diluted with 1,1,2-trichlorotrifluoroethane.   [b] From curve 2 of Fig. 1.

Attempts to vary the average chlorine concentration by changing its input rate gave, at most, minor changes in product ratios at mole fractions of olefin (0.07–0.20) at which radical and ionic processes are in competition. Hence, it appears that the most important factor causing the behavior shown in Table I is that the free-radical process is of higher kinetic order in cyclohexene than is the ionic process. We suggest that this high order in olefin results from participation of one or more molecules of cyclohexene in the initiation step, and that this spontaneous free-radical chlorination we have described is initiated by interaction of chlorine and cyclohexene to produce free radicals.[9] That initiation is not due to chance impurities is supported by several observations: (1) the percentage of radical reaction is not changed by

(9) Since chlorine is stable toward cyclohexane at 25° in the absence of light, initiation cannot be due to thermal dissociation of chlorine.

use of cyclohexene at progressive stages of purification, (2) it is not significantly changed by planned addition of suspected initiators such as hydroperoxides or substantially oxidized cyclohexene, and (3) the radical reaction still proceeds very rapidly at $-78°$. Such intermolecular "molecule-induced homolyses"[10] have been suggested in reactions of fluorine with aromatic compounds,[11] in the thermal polymerization of styrene,[12] and in the reaction of styrene with iodine[13]; this chlorine–cyclohexene reaction appears to be a particularly facile example of this class of reactions.

Preliminary results show that radical reactions also predominate during liquid phase chlorination of the isomeric butenes except for isobutylene, whose chlorination remains ionic. We hope later to report more fully on the structural factors determining the position of the ionic–radical balance for various olefins. At this point it seems obvious, however, that prediction of identities and ratios of products from liquid phase chlorination of olefins cannot be made on the basis of a single mechanism common to all olefins and media.

(10) J. C. Martin and E. H. Drew, *J. Am. Chem. Soc.*, **83**, 1232 (1961).
(11) W. T. Miller, Jr., S. D. Koch, Jr., and F. W. McLafferty, *ibid.*, **78**, 4992 (1956).
(12) F. Mayo, quoted in R. R. Hiatt and P. D. Bartlett, *ibid.*, **81**, 1149 (1959).
(13) G. Fraenkel and P. D. Bartlett, *ibid.*, **81**, 5582 (1959).

UNION CARBIDE RESEARCH INSTITUTE   MARVIN L. POUTSMA
UNION CARBIDE CORPORATION
TARRYTOWN, NEW YORK

Spin Densities in Tetrahedral Cobalt Complexes by Nuclear Magnetic Resonance Contact Shifts; Evidence for a Pseudo Contact Interaction

Sir:

We wish to report the observation of paramagnetic contact shifts in the n.m.r. spectra of aryl phosphine complexes of cobalt(II) dibromide. Resonances were observed for the *meta-* and *para-*hydrogens of bis-(triphenylphosphine)-dibromocobalt(II) and for the *meta-* and methyl-hydrogens of bis-(tri-*p*-tolylphosphine)-dibromocobalt(II). The peak for the *para-*hydrogen was shifted upfield while the peaks for the *meta-* and methyl-hydrogens were shifted to lower fields with respect to their positions in the diamagnetic ligands. No observable *ortho-*hydrogen resonance has so far been located. Our chemical shifts are similar in character to those recently observed[1–4] in some paramagnetic Ni(II) chelates. The observed half-width of our resonance peaks is about 20 c.p.s. at room temperature and the lines become even sharper as the temperature is lowered. Our spectra were recorded on a Varian n.m.r. spectrometer operating at 60 Mc./sec. on $CDCl_3$ solutions of the complexes with the $CHCl_3$ resonance taken as an internal standard. The temperature was varied from $-64°$ to $+55°$. Using eq. 1[2,5] to obtain the hyperfine contact interaction constants, a_i, from the temperature dependence of the spectra, and relating these to the spin densities, ρ_i,

(1) D. R. Eaton, A. D. Josey, W. D. Phillips, and R. E. Benson, *J. Chem. Phys.*, **37**, 347 (1962).
(2) D. R. Eaton, A. D. Josey, W. D. Phillips, and R. E. Benson, *Discussions Faraday Soc.*, **34**, 77 (1962).
(3) D. R. Eaton, A. D. Josey, R. E. Benson, W. D. Phillips, and T. L. Cairns, *J. Am. Chem. Soc.*, **84**, 4100 (1962).
(4) D. R. Eaton, W. D. Phillips, and D. J. Caldwell, *ibid.*, **85**, 397 (1963).
(5) H. M. McConnell and C. H. Holm, *J. Chem. Phys.*, **27**, 314 (1957).

$$\left(\frac{\Delta H}{H}\right)_j = -a_j \frac{\gamma_e}{\gamma_H} \frac{g\beta S(S+1)}{6kT} \tag{1}$$

on the aromatic carbon atoms by eq. 2[6] we obtained the

$$a_j = Q\rho_j \tag{2}$$

results shown in Table I. Also given are the observed room temperature shifts.

TABLE I

RESULTS FROM EQUATIONS 1 AND 2

	$\Delta H_j{}^a$	$a_j{}^b$	$\rho_j{}^c$
Co[P(C$_6$H$_5$)$_3$]$_2$Br$_2$			
meta-H	−486.2	+0.0403	−0.00179
para-H	+720.2	− .0521	+ .00231
Co[P(C$_3$H$_7$)$_3$]$_2$Br$_2$			
meta-H	−486.9	+ .0407	− .00181
−CH$_3$	−721.4	+ .0559	

^{a} Shifts in c.p.s. at 25°.　^{b} Gauss.　^{c} $Q_{CH} = -22.5$ gauss.

The triphenylphosphine complex, described by Cotton and co-workers[7] contains tetrahedrally coordinated cobalt(II). Magnetic measurements[7] indicate that the cobalt is in an $S = {}^3/_2$ state and from $\mu_{eff} = 4.52$ Bohr magnetons we estimate a g-factor of 2.33. The temperature dependences of the meta- and para-hydrogen resonance shifts in Co[P(C$_6$H$_5$)$_3$]$_2$Br$_2$ are shown in Fig. 1. The linearity of these plots indicates that no free energy term such as used by Eaton, et al.,[1-4] in the analysis of the spectra of Ni(II) aminotroponeimineates is necessary. These cobalt phospine complexes have a spin free d^7 configuration and no diamagnetic–paramagnetic equilibrium is possible.

Previous work[3,8] has indicated that substitution of a methyl group for a hydrogen at various positions on a phenyl ring does not appreciably alter the spin densities at the aromatic carbon atoms. In our case, if we assume no change in the ratio of spin densities between the meta and para positions in the phenyl and p-tolyl derivatives, we obtain a value of Q_{CH_3} of 23.9 gauss from the observed shift of the methyl resonance. This value is lower than that found from e.s.r.[9] measurements and in the N-substituted p-tolyl derivative of Ni(II) aminotroponeimineate.[3] The work of Eaton, et al.,[3] indicates that in paramagnetic conjugated systems containing methyl groups, Q_{CH_3} varies considerably, and this variation is attributed to differences in the size of the conjugated system to which the methyl group finds itself attached. Spectroscopic evidence[10] indicates that in coordinated triphenylphosphine the phenyl groups are not conjugated with one another.

We were, however, able to obtain identical spin densities at the para-carbon atom in both the phenyl- and p-tolylphosphine complexes with larger values of Q_{CH_3} by considering a pseudo contact interaction.[3,11,12] This interaction causes a shift of all resonances in proportion to the reciprocals of the cubes of the distance of the resonating nuclei from the paramagnetic ion. For example, a pseudo contact interaction which at 25° produces an upfield shift of the meta-hydrogen resonance 60 c.p.s., the para-hydrogen 40 c.p.s., and the methyl-hydrogens 27 c.p.s., yields a Q_{CH_3} of +27.0 gauss. The actual value of Q_{CH_3} in our system is, of

Fig. 1.—Fractional observed shifts for meta- and para-hydrogens in Co[P(C$_6$H$_5$)$_3$]$_2$Br$_2$ vs. $1/T$.

course, unknown and further work is indicated, but it is not unlikely that there is some pseudo contact contribution to the observed resonance shifts. We expect the pseudo contact interaction to be large when there is a large anisotropy in the g-value. Due to the dissimilarity in ligands and their positions in the spectrochemical series[7] a fairly large C_{2v} component in the ligand field is not unlikely; this is consistent with a moderately anisotropic g-value. The ratio of the absolute values of the para spin density to the meta spin density is lower than found for most of the compounds measured by Eaton, et al.,[1-4] but it may be significant that the ratio is fairly close to that found in a chelate containing a phenyl group bonded to a sulfur atom.[1]

We have observed resonances in other tetrahedral cobalt complexes and in the analogous nickel compounds. Arsine and phosphine oxide complexes are being investigated and the results will be reported in a subsequent publication.

DEPARTMENT OF CHEMISTRY　　　　　W. D. HORROCKS, JR.
PRINCETON UNIVERSITY　　　　　　　G. N. LA MAR
PRINCETON, NEW JERSEY

(6) H. M. McConnell, J. Chem. Phys., 24, 632 (1956).

(7) F. A. Cotton, O. D. Faut, D. M. L. Goodgame, and R. H. Holm, J. Am. Chem. Soc., 83, 1780 (1961).

(8) J. R. Boulton, A. Carrington, and A. D. McLachlan, Mol. Phys., 5, 31 (1962).

(9) R. W. Fessenden and R. H. Schuler, J. Chem. Phys., 33, 935 (1960).

(10) H. H. Jaffé, ibid., 22, 1430 (1954).

(11) H. M. McConnell and R. E. Robertson, ibid., 29, 1361 (1958).

(12) Subsequent to submitting this communication an article appeared [J. A. Happe and R. L. Ward, ibid., 39, 1211 (1963)] wherein pseudo contact shifts in octahedrally coordinated Co(II) complexes were reported.
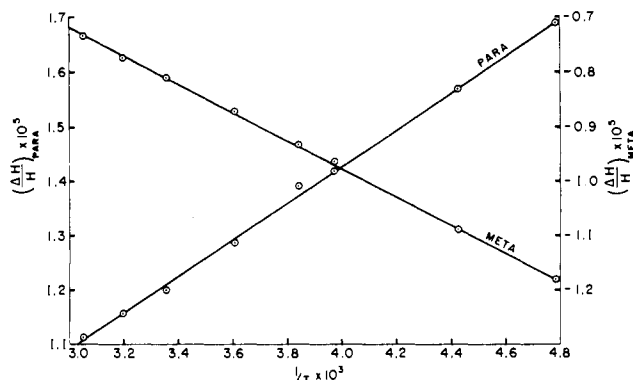
The Esterolytic Catalysis of Poly-4(5)-vinylimidazole and Poly-5(6)-vinylbenzimidazole

Sir:

We wish to report an unusual catalytic effect of poly-4(5)-vinylimidazole and poly-5(6)-vinylbenzimidazole.

The role of imidazole in the multifunctional catalysis of chymotrypsin has been recognized.[1] pH–rate profiles of chymotrypsin have sigmoid or bell-shaped curves. Recently a sigmoid profile has been identified with a rate-determining deacylation step, involving one functional group (probably imidazole).[2] A bell-shaped curve has been identified with a rate-determining acylation step in which a second group besides imidazole is involved.[2] This group may be the hydroxyl group

(1) H. Gutfreund and J. M. Sturtevant, Biochem. J., 63, 656 (1956); L. Weil, S. James, and A. R. Buchert, Arch. Biochem. Biophys., 46, 266 (1953); J. R. Whitaker and B. J. Jandorf, J. Biol. Chem., 223, 751 (1956); V. Massey and B. S. Hartley, Biochim. Biophys. Acta, 21, 361 (1956); G. Schoellmann and E. N. Shaw, Biochemistry, 2, 252 (1962). For a review see J. A. Cohen, R. A. Oosterbaan, H. S. Jansz, and F. Berends, J. Cellular Comp. Physiol., 54, 231 (1959); E. A. Barnard and W. D. Stein, "Advances in Enzymology," Vol. 20, F. F. Nord, Ed., Interscience Publishers, Inc., New York, N. Y., 1958, p. 51.

(2) M. L. Bender, G. E. Clement, F. J. Kézdy, and B. Zerner, J. Am. Chem. Soc., 85, 358 (1963).