CH₂Cl₂ indicates that both high-spin and low-spin species are present in this solvent. Moreover, in view of the above it is tempting to postulate a planar structure for the low-spin compound.

The infrared spectrum of solid [Co(PEt₃)₂(NCS)₂] in Nujol mull shows a strong band at 2090 cm.$^{-1}$ assigned to the CN stretching vibration of the SCN group and does not have absorption bands in the 2130–2160-cm.$^{-1}$ region. The possibility that the metal may effectively be six-coordinated through SCN groups seems in this case to be ruled out. It is worth noting that the CN stretching frequency of *trans*-[Ni(PEt₃)₂(NCS)₂] has the same value of 2090 cm.$^{-1}$. The two strong bands observed at 830 and 795 cm.$^{-1}$ in the spectrum of [Co(PEt₃)₂(NCS)₂] but absent in the spectra of [Co(PEt₃)₂Cl₂] and [Co(PEt₃)₂Br₂] are assigned to the CS (pseudo-symmetrical N–C–S) stretching vibration of the CNS group in isothiocyanates.[6] The doublet structure might arise either from a *cis*- or from a distorted *trans*-planar configuration. Similar conclusions apply to the infrared spectra in CH₂Cl₂ solution. In particular the spectra of 0.25 *M* solutions in this solvent exhibit bands having the integral intensity of coordinate isothiocyanate groups.

Conductivity measurements were made in CH₂Cl₂ at 25° at a concentration of 10^{-3} *M*. The small conductivity (<0.9 ohm^{-1} cm.$^{-2}$ mole^{-1}) indicates that the complex is a nonelectrolyte in CH₂Cl₂ and could arise from partial rearrangement in solution to the ionic form [Co(PEt₃)₄][Co(NCS)₄] (Λ_M found for 1.8 × 10^{-3} *M* N(C₂H₅)₄Br, 13.2).

The X-ray powder pattern of [Co(PEt₃)₂(NCS)₂], as it differs considerably from those obtained for the tetrahedral [Zn(PEt₃)₂(NCS)₂] as well as for the planar *trans*-[Ni(PEt₃)₂(NCS)₂] and *cis*-[Pt(PEt₃)₂(NCS)₂], is not of great help in establishing the structure of the compound.

A reasonable conclusion which can be drawn from the combined analytical, conductance, spectral, and magnetic data is that [Co(PEt₃)₂(NCS)₂] is an example of conformational isomerism between a low-spin (probably planar) and a high-spin (tetrahedral) form.

This problem is being further investigated and detailed reports will follow.

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(6) A. Turco and C. Pecile, *Nature*, **191**, 66 (1961).

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Competition Between Ionic and Free-Radical Reactions during Chlorination of Cyclohexene. Spontaneous Generation of Radicals

Sir:

Although considerable evidence suggests that chlorination of olefins in polar solvents involves electrophilic attack by chlorine,[1] the mechanism of chlorination in nonpolar solvents has not been as extensively studied. Such chlorinations produce both addition and substitution products.[2] Taft[3] has attempted to correlate the addition–substitution ratio with olefin structure on the basis of ionic intermediates; indeed, labeling experiments strongly suggest that chlorination of iso-

butylene proceeds by an ionic pathway.[4] However, several workers[5] have observed that chlorination of an olefin can induce chlorination of paraffinic solvents; these reactions appear to involve free-radical chain reactions. We wish to report some of our studies on chlorination of cyclohexene which shed light on this apparent anomaly.

Passage of chlorine diluted with nitrogen into cyclohexene in the *absence of light* at 25.0° produces in a rapid reaction[6] three major products: 1,2-dichlorocyclohexane (I),[7] 3-chlorocyclohexene (II), and 4-chlorocyclohexene (III)[8]; admixture with cyclohexane leads to considerable chlorocyclohexane (IV). Use of oxygen as a carrier gas eliminates III (and IV with cyclohexane present), whereas I and II are produced in a
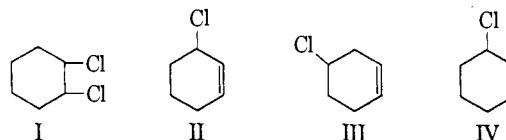
still rapid reaction[6]; use of polar solvents such as acetonitrile also eliminates III and IV. This behavior suggests the existence of both an ionic pathway producing I and II and a radical pathway producing I, II, and III.

Chlorination of cyclohexene diluted with 1,1,2-trichlorotrifluoroethane at low conversion (0.2–0.8 mmole of chlorine per 15 ml. of reaction mixture) gave the striking results plotted in Fig. 1; analysis was by temperature-programmed g.l.c. on a polypropylene glycol column. As dilution increased, chlorination under nitrogen in the absence of light gave constant ratios of III/II and I/II down to a mole fraction of olefin of ~0.40 followed by a sharp decrease of III/II toward zero at infinite dilution and a simultaneous less dramatic increase in I/II (curves 2 and 5). We therefore feel that at mole fractions >0.40 the reaction is almost exclusively radical, whereas at lower concentrations of olefin the ionic reaction becomes predominant. Consistent with this view is the fact that illumination (three 275-watt sunlamps at 6–9 in. through Pyrex) did not change the III/II and I/II ratios at high concentration (the expected result only if reaction were already entirely radical), but did practically eliminate the changes in III/II and I/II at low concentration (curves 3 and 4). If we assume that the radical process produces I, II, and III in the ratio 1.95:1.00:0.60 (the high concentration limit) and that the ionic process produces I and II in the same ratio under nitrogen as under oxygen at a given concentration of olefin (curve 1), the observed III/II ratios can be used to calculate the percentage of radical reaction (*r*) at each concentration and the corresponding value of I/II based on this *r* and the previous assumptions (Table I). The calculated results for I/II agree with the observed values within the apparent experimental error; to this extent the assumption that the radical yield ratio (1.95: 1.00:0.60) is independent of dilution is confirmed.

Use of cyclohexane as diluent gave comparable results for cyclohexene-derived products and also allowed determination of the relative reactivities of a 4-cyclohexenyl hydrogen atom and a cyclohexyl hydro-

(1) P. B. D. de la Mare, *Quart. Rev.* (London), **3**, 126 (1949).

(2) See, for example, H. P. A. Groll, G. Hearne, F. F. Rust, and W. E. Vaughan, *Ind. Eng. Chem.*, **31**, 1239 (1939); D. V. Tishchenko, *J. Gen. Chem. USSR*, **8**, 1232 (1938).

(3) R. W. Taft, Jr., *J. Am. Chem. Soc.*, **70**, 3364 (1948).

(4) W. Reeve, D. H. Chambers, and C. S. Prickett, *ibid.*, **74**, 5369 (1952).

(5) (a) T. D. Stewart and D. M. Smith, *ibid.*, **51**, 3082 (1929); (b) T. D. Stewart and M. H. Hanson, *ibid.*, **53**, 1121 (1931); (c) T. D. Stewart and B. Weidenbaum, *ibid.*, **57**, 2036 (1935); (d) T. D. Stewart and B. Weidenbaum, *ibid.*, **58**, 98 (1936); (e) J. C. Kuriacose, *Indian J. Appl. Chem.*, **22**, 181 (1959).

(6) No visual build-up of chlorine in solution.

(7) This product was >99% *trans* in reactions described herein as ionic, but up to 4% *cis* in those described as radical.

(8) Suggested as a product without isolation or positive identification by G. F. Bloomfield, *J. Chem. Soc.*, 114 (1944).
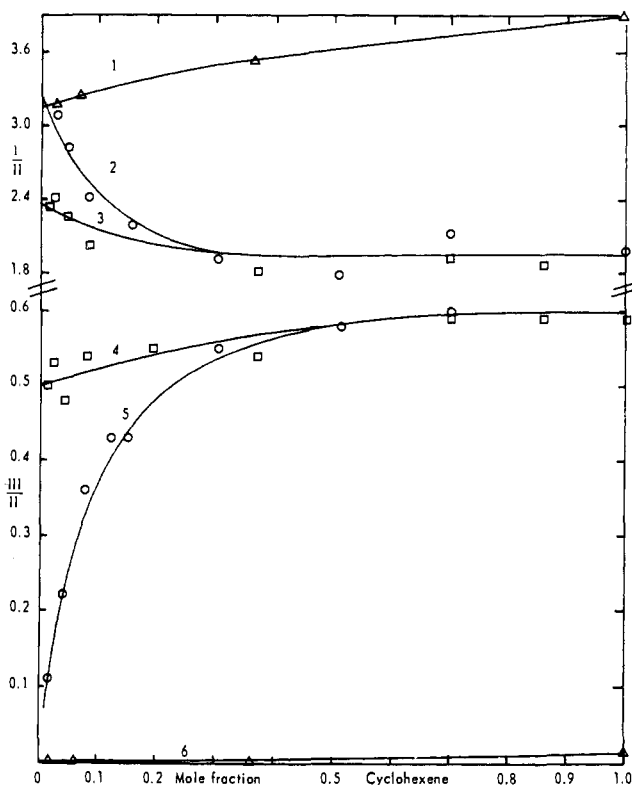
Fig. 1.—Variation of product ratios with concentration during chlorination of cyclohexene at 25.0°: ○, nitrogen in the dark; ▢ nitrogen with illumination; △, oxygen in the dark.

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.

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(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).

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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 CDCl₃ solutions of the complexes with the CHCl₃ 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,

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