g. (55% yield) of *trans*-5-decene. The infrared spectrum of the main fraction of the product (b.p. 170° at 746 mm., $n^{20}\mathrm{D}$ 1.4247, f.p. −71 to −72° cor.) was identical to that of a sample of authentic *trans*-5-decene; characteristic peaks of *cis*-5-decene were entirely absent.

B. **At +17°.**—Two-tenths of a mole of 5-decyne was added dropwise over two hours to a solution of 5.5 g. (0.8 g. atom) of lithium in 300 cc. of ethylamine in a flask equipped with a stirrer, a dropping funnel and a Dry Ice condenser. A Drierite tube was used to exclude water; no insulation or cooling baths were placed around the flask. Stirring was continued for ten hours. The blue reaction mixture was then packed in Dry Ice overnight and then permitted to warm up to 17° the next day. More lithium (1.94 g.) was added; the color of the solution changed from colorless through a pink to a permanent blue in one hour. After four more hours of stirring, the remaining pieces of lithium were removed and solid ammonium chloride was added until the solution was colorless. The product was then taken up in low-boiling petroleum ether, as in the reduction at −78°. The petroleum ether solution was treated with an excess of bromine dissolved in carbon tetrachloride, washed with sulfurous acid and water, and dried. The solvent was evaporated and the residue was distilled. The distillate (b.p. 60–70° at 18 mm., $n^{20}\mathrm{D}$ 1.4149) was treated with sodium at 110° for two hours. The hydrocarbon was separated from the sodium by vacuum distillation to give 5.5 g. (19% yield) of pure *n*-decane,[5] b.p. 66–67° (18 mm.), $n^{20}\mathrm{D}$ 1.4120, f.p. −30° cor.

C. **At +17°.**—One-tenth mole of 5-decyne was added dropwise over one hour to a stirred solution of 2.08 g. (0.3 g. atom) of lithium in 300 cc. of ethylamine. Ten grams of methanol was added after 2.3 hours more of stirring. The product was isolated and purified as in the reduction at −78°. Eight grams of impure product (assumed to be a mixture of *n*-decane and *trans*-5-decene) was obtained upon fractional distillation; the boiling points of the fractions varied from 168 to 170.9° at 747 mm. while the refractive indices varied from $n^{20}\mathrm{D}$ 1.4219 to 1.4200. The infrared spectrum indicated that *trans*-5-decene was the only olefin isomer present in the mixture.

Reduction of 3-Octyne with Lithium in Ethylamine at −78°.—Twenty-two grams (0.2 mole) of 3-octyne was treated with 3.45 g. (0.5 g. atom) of lithium in 300 cc. of ethylamine for two hours at about −78° and then methanol was added to destroy the excess lithium. The yield of *trans*-3-octene was 52% (11.65 g.), b.p. 122.2° at 754 mm., $n^{20}\mathrm{D}$ 1.4130, initial f.p. −110.4°, purity 98.2 mole %. Its infrared spectrum was identical to that of an authentic sample of *trans*-3-octene; peaks characteristic of *cis* 3-octene were absent entirely.

Preparation of Authentic Samples of the *cis* and *trans* Isomers of 5-Decene and 3-Octene.[3]—The corresponding dialkylacetylenes were hydrogenated in the presence of Raney nickel to give the *cis*-olefins and reduced with sodium in ammonia to give the *trans*-olefins: *trans*-5-decene, yield 60%, b.p. 170–170.5° at 753 mm., $n^{20}\mathrm{D}$ 1.4240, f.p. −72° cor.; *cis*-5-decene, yield 72%, b.p. 170° at 752 mm., $n^{20}\mathrm{D}$ 1.4256, f.p. −113° cor.; *trans*-3-octene, yield 71%, b.p. 122.5° at 751 mm., $n^{20}\mathrm{D}$ 1.4132, initial f.p. −109.09°, purity 99.5 mole %; *cis*-3-octene, yield 59%, b.p. 121–121.5° at 748 mm., $n^{20}\mathrm{D}$ 1.4137, very wide freezing point range.[6]

Attempted Isomerization of *cis*-5-Decene.—Benzene (6.85 g.) was added dropwise to a solution of 2.43 g. of lithium in ethylamine.[1] After the lithium had been completely consumed in the reduction, *cis*-5-decene was added. The mixture was stirred for four hours, methanol was added and the decene was isolated in the usual way; $n^{20}\mathrm{D}$ 1.4252. The recovered decene then was added to a solution of lithium in ethylamine which was kept at Dry Ice temperature. The solid lithium was removed after 2.5 hours and methanol was added. The decene was isolated in the usual manner; b.p. 169° (753 mm.), $n^{20}\mathrm{D}$ 1.4250. The infrared spectra before and after attempted isomerization were identical.

Freezing Points.—The freezing points of the *trans*-3-octenes were secured with the aid of a platinum resistance thermometer[7] and may therefore be considered very accurate. The other freezing points were obtained with the aid of a pentane thermometer which had been calibrated with powdered Dry Ice; their probable accuracy was considered to be ±1°.

Reduction of Cyclohexane by Lithium in Ethylamine. A. **At 17°.**—Treatment of 16.4 g. (0.20 mole) of cyclohexene with 4.2 g. (0.6 g. atom) of lithium in 200 cc. of ethylamine resulted in 8.50 g. (51%) of cyclohexane, b.p. 79–80° (743 mm.), $n^{20}\mathrm{D}$ 1.4260. The solution decolorized bromide only slowly in carbon tetrachloride and slowly gave a red color with fuming sulfuric acid indicating only a trace of cyclohexene if any.

B. **At −78°.**—The treatment of 16.4 g. (0.2 mole) of cyclohexene with 4.2 g. (0.6 g. atom) of lithium in ethylamine at −78° after working up the reaction mixture resulted in the recovery of the cyclohexene essentially unchanged.

Determination of Absorption of Lithium by Cyclohexene in Ethylamine.—Employing the technique previously described,[8] the metal to hydrocarbon ratio between lithium and cyclohexene was determined in order to distinguish between an addition mechanism or reduction by "nascent" hydrogen for the isolated double bond. Triplicate determinations indicated an uptake of 2.0, 1.5 and 1.9 equivalents of lithium per mole of hydrocarbon.

Reduction of 1-Ethylcyclohexene by Lithium in Ethylamine.—The reduction of 16.9 g. (0.154 mole) of 1-ethylcyclohexene by 3.2 g. (0.46 g. atom) of lithium in 250 cc. of ethylamine resulted in 11.6 g. (68%) of a mixture of 1-ethylcyclohexene and ethylcyclohexane, $n^{20}\mathrm{D}$ 1.4482. The mixture was analyzed refractometrically and found to contain 62% olefin and 38% ethylcyclohexane.

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[5] K. N. Campbell and L. T. Eby, THIS JOURNAL, **63**, 2684 (1941).

[6] A similar observation on the f.p. of this compound was made by A. L. Henne, see *ibid.*, **65**, 2020 (1943).

[7] The authors wish to thank Mr. H. Podall of the Purdue Chemistry Department for his assistance in this matter.

[8] R. A. Benkeser, R. E. Robinson and H. Landesman, THIS JOURNAL, **74**, 5701 (1952).

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Dealkylation of Diisopropyl Phosphite by Hydrogen Chloride[1]

BY C. H. CAMPBELL[2] AND D. H. CHADWICK[2]

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Gerrard and Whitbread have reported a study of the dealkylation by hydrogen halide of the *n*-butyl phosphites.[3] They examined their data with a view to calculating specific rates. They concluded, and we agree, that study over a much more extensive field of conditions is necessary before precise statements can be made about the details of mechanism. Toward this end, it appears worth while to report pertinent data obtained by us in connection with another problem.

Solutions of hydrogen chloride of 4 to 7% by weight in diisopropyl phosphite were prepared, and the rate of dealkylation at room temperature and at 40° followed by titrating aliquots of the solutions for ionic chloride by the modified Volhard method. The data obtained, presented in Table I, are in excellent agreement with second-order kinetics in respect to hydrogen chloride. The data are not in agreement with first-order kinetics in respect to

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[1] This paper reports work done under contract with the Chemical Corps, U. S. Army, Washington 25, D. C., in the Research Laboratory of the Former Phosphate Division, Monsanto Chemical Co., Anniston, Alabama.

[2] Organic Chemicals Division, Monsanto Chemical Co., St. Louis, Mo.

[3] W. Gerrard and E. G. G. Whitbread, *J. Chem. Soc.*, 914 (1952).

hydrogen chloride, as might be predicted on the basis of the straight-forward reaction mechanism $(C_3H_7O)_2POH + HCl \rightarrow C_3H_7OP(OH)_2 + C_3H_7Cl$ under conditions of a large excess of phosphite.

TABLE I

CLEAVAGE OF DIISOPROPYL PHOSPHITE BY HYDROGEN CHLORIDE

Time, hours	First-order rate constant[a] $K = \frac{1}{t}\ln\frac{C_0}{C}$ $\times 10^6$	Second-order rate constant[a] $K = \frac{1}{t}\left(\frac{1}{C} - \frac{1}{C_0}\right)$ $\times 10^6$
	At room temperature (25°)	
0	...	...
1	...	...
2	8.09	6.18
19	2.34	1.88
25	2.18	1.79
140.3	1.64	1.89
165.3	1.53	1.85
192	1.48	1.92
259	1.34	1.98
	Average of six values[b]	1.89
	At 40°	
0	...	...
1	20.1	10.9
3	10.9	6.1
5.5	15.7	9.7
6.4	15.3	9.7
7	15.0	9.6
24	11.6	10.5
26	11.2	10.4
28	10.9	10.4
30	10.7	10.6
31	10.5	10.6
	Average of eight values[b]	10.2

[a] Calculated from densities of $(C_3H_7O)_2POH$ of 0.992 and 0.978, and neglecting volume and weight changes due to HCl and reaction products. Units of specific rate constants are sec.$^{-1}$ and liter mole^{-1} sec.$^{-1}$. [b] Values of K at times of less than three hours were not averaged since experimental errors show a comparatively great effect during the initial period of reaction. It may also be that attainment of the equilibrium suggested below is a factor.

That the alkyl phosphites form complexes with hydrogen halides is generally accepted; the hydrogen halides dissolve in dialkyl phosphites with considerable evolution of heat, and are difficult to remove by application of reduced pressure or by sweeping with an inert gas. We observed a heat of solution of 10.7 kcal./mole for the solution of hydrogen chloride in an excess of diisopropyl phosphite (mole ratio of *ca.* $^1/_{160}$) at 25 to 30°.

If it is assumed that dealkylation of the dialkyl phosphites takes place by attack of hydrogen halide on a phosphite–hydrogen halide complex, second-order kinetics in respect to hydrogen chloride might be expected: Assume

$$(RO)_2POH + HCl \rightleftarrows (RO)_2POH\cdot HCl$$

$$(RO)_2POH\cdot HCl + HCl \longrightarrow ROP(OH)_2\cdot HCl + RCl$$

Then, letting $[HCl]_F$ and $[HCl]_T$ represent the concentrations of free and total hydrogen chloride, respectively,

$$-d[HCl]_F/dt = K[(RO)_2POH\cdot HCl][HCl]_F$$

and

$$K_e = [(RO)_2POH\cdot HCl]/[(RO)_2POH]_F[HCl]_F$$

so

$$-d(HCl)_F/dt = KK_e[(RO)_2POH]_F[HCl]^2{}_F$$

Since

$$[(RO)_2POH] >> [HCl]$$

it is essentially constant and

$$-d[HCl]_F/dt = K'[HCl]^2{}_F$$

Then

$$[HCl]_T = [(RO)_2POH\cdot HCl] + [HCl]_F$$
$$[HCl]_T = K_e[(RO)_2POH]_F[HCl]_F + [HCl]_F$$
$$[HCl]_T = [HCl]_F(K'')$$

and

$$-d[HCl]_T/dt = K'''[HCl]^2{}_T$$

The condition of an excess of dialkyl phosphite in our experiments not only permits simplification in deriving the kinetics for the proposed mechanism, but also tends to minimize the effects of two complicating factors: (1) the consecutive reaction

$$ROP(OH)_2 + HCl \rightleftarrows ROP(OH)_2\cdot HCl \xrightarrow{HCl} P(OH)_3 + RCl$$

and (2) the equilibrium[4]

$$(RO)_2POH + P(OH)_3 \rightleftarrows 2ROP(OH)_2$$

Employing the Arrhenius equation and the specific rate constants determined at 25° and at 40°, the energy of activation for the cleavage of diisopropyl phosphite by hydrogen chloride is calculated to be 20.9 kcal. per mole.

We wish to thank Dr. G. B. Kistiakowsky for his helpful suggestions.

[4] D. H. Chadwick, P. A. Sanguinetti and E. E. Hardy, presented at the 122nd National Meeting of the American Chemical Society, Atlantic City, N. J., Sept., 1952.

ST. LOUIS, MISSOURI

Air Oxidation of Hydrocarbons. IV. The Effects of Varying Solvent and the Mechanism of Uninhibited Chain Termination

BY CHARLES E. BOOZER, GEORGE S. HAMMOND, CHESTER E HAMILTON AND CONRAD PETERSON

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In the previous papers in this series we have shown that in benzene and chlorobenzene the inhibition of cumene and tetralin oxidation can be accommodated by a consistent picture as to the mechanism of the inhibition reactions. In the course of this study we have made other observations, mainly concerned with oxidation in other solvents, which are less complete but are considered to be of sufficient interest to be reported at the present time. The results include some interesting deviant behavior for which no good explanation can be offered at the present time.

Results and Discussion

Rates of Uninhibited Oxidation.—The rate of initiated oxidation at partial pressures of oxygen which are high enough to make the reaction zero order with respect to oxygen and in the absence of