Table I lists relative intensities of some of the larger peaks in the mass spectra obtained with ionizing voltages of 70, 20 and 12 v. The mass spectrum at 70 v. is extremely complicated, with peaks at almost every mass number from 24 to 222. At low voltage the spectrum becomes simpler and only the heavier fragment ions are observed. The relative intensity of the isotope peaks indicates the number of boron atoms in each fragment ion or, at least, sets an upper limit to the number. (B^{10} is 0.25 × B^{11}, $B^{10}B^{11}$ is 0.50 × $B_2{}^{11}$ and $B^{10}B_2{}^{11}$ is 0.75 × $B_3{}^{11}$.) Thus, it is found that the ion of mass 208 cannot contain three boron atoms and must be the fragment ion indicated in the last column. Table I gives in the last column the probable chemical formulas of some of the ions, but formulas enclosed in parentheses are open to some uncertainty as there are alternative possibilities.

TABLE I

PARTIAL MASS SPECTRUM OF $(P(CH_3)_2BH_2)_3$

Mass	Relative intensity 70 v.	20 v.	12 v.	Positive ion
27	65	0	0	$B^{11}CH_4$
41	100	0	0	$B^{11}(CH_3)_2$
75	23.6	0.5	0	$(P(CH_3)_2B^{11}H_3)$
89	27.1	2.0	0	$(P(CH_3)_3B^{11}H_2)$
131	14.6	3.2	0	
136	13.4	4.6	0	$P_2(CH_3)_4B^{11}H_3$
145	21.6	6.1	0	$(P_2(CH_3)_4B_2{}^{11}H)$
161	53.6	28.2	6.9	$(P_2(CH_3)_4B_3{}^{11}H_6)$
178	10.3	8.3	6.9	
205	19.8	11.4	6.5	
208	17.5	11.0	3.0	$P_3(CH_3)_6B_2{}^{11}H_3$
220	47.1	29.6	9.3	$P_3(CH_3)_6B_3{}^{11}H_4$
222	18.6	10.0	4.2	$P_3(CH_3)_6B_3{}^{11}H_6$

This is an unusual spectrum in several respects. The most abundant ion in the 70 v. spectrum, $B(CH_3)_2{}^+$, involves a very unusual type of rearrangement in the ionization process and it has a very high appearance potential of over 20 v. It is of interest that the fragment ions of mass 208 and mass 161 appear below 12 v. ionizing potential, for these fragment ions involve breaking the ring and breaking another P–B bond in the ionization process.

2. Pyrolysis Studies

A static technique was used in which samples of 2.0 mg. were sealed in evacuated 10-ml. ampules designed so that they could be broken and the products led into the mass spectrometer. These ampules containing the samples were heated in a muffle furnace for various times of from 1 to 5 hours at temperatures ranging from 251 to 510°. Products were then examined mass spectrometrically.

Very little decomposition if any occurred in 4 hours at 251°. At 360° hydrogen was gradually evolved, reaching 0.35 mole H_2 per mole of trimer in 5 hours, and was accompanied by very small amounts of methane. At 510° the identified products were hydrogen, methane, ethane and elemental phosphorus, found in the ratio of approximately 0.5 mole, 1 mole, 0.2 mole and 1 gram-atom per mole of trimer used, and liberated mainly during the first hour of pyrolysis. The amount of phosphorus present may have been much greater than observed because of incomplete vaporization into the mass spectrometer inlet reservoir. Peaks characteristic of the original trimer were observed in all cases but were very much diminished in intensity in the experiments at 510°. In the latter experiments the appearance of a $B^{11}(CH_3)_2{}^+$ peak also strongly suggests the formation of methyl derivatives of mixed boranes. This and the production of large amounts of phosphorus indicate a relocation of the methyl groups during pyrolysis.

The relative intensities in the spectrum of phosphorus vapor are as follows: $P_1{}^+$ 20, $P_2{}^+$ 26, $P_3{}^+$ 7.6, $P_4{}^+$ 100. The sensitivity to the $P_4{}^+$ ion is about 0.5 times the sensitivity of the mass 43 peak of *n*-butane. A spectrum obtained in a different type of mass spectrometer has been described by Dukelskii and Zandberg.[3]

The thermal decomposition data indicate that the dimethylphosphinoborine trimer does not depolymerize into its monomer but decomposes in a more complicated manner. The decomposition appears to occur in two stages: (1) at 360° liberation of hydrogen and small amounts of methane with possible ring condensation and (2) at 510° destruction of the ring and relocation of the methyl groups with the formation of elemental phosphorus and methyl derivatives of the boranes. This migration of methyl groups also occurs in the mass spectra as noted above.

For a coördination compound this material has an unusual degree of stability, as indicated by both the mass spectrometer and thermal results.

(3) V. M. Dukelskii and E. Ya. Zandberg, *Doklady Akad. Nauk. S.S.S.R.*, **86**, 263 (1952).

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Homogeneous Catalytic Hydrogenation. II. The Effect of Catalyst Environment on the Activation of Molecular Hydrogen

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A number of investigators have reported the homogeneous catalytic activation of hydrogen[1-3] by cuprous acetate in quinoline. We wish to report the effects obtained by altering the coördination sphere around the metal atom by chelation. Ethylenediamine (en) and ethylenediaminetetraacetic acid (enta) inhibit both the rate and extent of reduction of *p*-benzoquinone and cupric acetate monohydrate in quinoline solution at 100° (Table I). The magnitude of the inhibition increases with increasing concentration of the chelating agent (*e.g.*, runs 372, 293; 364, 352). The effect on the reduction of cupric acetate monohydrate is less, at a given level of chelating agent concentration, than on the reduction of quinone (runs 372, 409).

A quinoline solution of cuprous acetate alone is relatively stable toward hydrogenation (run 485). However, the reduction of cuprous acetate to metallic copper is catalyzed by reduced quinone (run 287), en (run 371), and cystine (run 466), but not by enta (runs 364, 352, 408).

When a mixture of cupric acetate monohydrate and *p*-benzoquinone was reduced in the absence of enta, the usual reduction of cuprous acetate to metallic copper after the break point (Table I, run 251) occurred (Fig. 1A). When enta was present (Fig. 1B), however, the reduction of cuprous acetate to copper metal was prevented.

(1) M. Calvin, *Trans. Faraday Soc.*, **34**, 1181 (1938)
(2) Sol Weller and G. A. Mills, THIS JOURNAL, **75**, 769 (1953).
(3) W. K. Wilmarth and Max K. Barth, *ibid.*, **75**, 2237 (1953)

TABLE I

THE EFFECT OF CHELATING AGENTS ON THE CUPROUS ACETATE CATALYZED REDUCTION OF *p*-BENZOQUINONE OR CUPRIC ACETATE MONOHYDRATE AT 100°

Reaction conditions: 2.0 millimoles substrate, 515 mm. H_2, 40 cc. of quinoline

Run	Substrate[a]	Chelating agent[b]	CuAc, mmoles	Chelating agent, mmoles	Reacn. time, min.	Reduction rate[c]	Redn. of substrate,[d] %	Redn. of CuAc, %	Remarks
251	Quinone	.....	2.6	...	200	0.6	75	0[e], 23[f]	Std. quinone redn.
485	.....	.....	2.7	...	150	.0	..	0	Stability of cuprous acetate
371	.....	En	2.9	0.92	140	.7	..	33	H_2 absorbed; copper pptd.
372	Quinone	En	2.9	0.90	70	.4	12	1	
293	Quinone	En	2.8	10.0	45	.0	0	0	Complete inhibition
375[b]	$CuAc_2$	.....	2.8	....	48	.7	100	0	No copper pptd.
409	$CuAc_2$	En	2.4	0.93	76	.7	89	0	No copper pptd.
418	$CuAc_2$	En	2.5	2.6	115	.8	80	24	Copper pptd.
410	$CuAc_2$	En	3.4	5.5	110	.5	8	28	Copper pptd.
364	Quinone	Enta	3.0	0.25	100	.6	66	0	No copper pptd.
352	Quinone	Enta	2.5	.50	145	.2	39	0	No copper pptd.
408	Quinone	Enta	2.4	.50	136	.3	37	0	No copper pptd.
413	$CuAc_2$	Enta	2.4	.50	80	.6	84	3	
466	.....	Cystine	2.7		80	.3	..	55	H_2 absorbed; copper pptd.

[a] Quinone = *p*-benzoquinone, $CuAc_2$ = cupric acetate monohydrate. [b] en = ethylenediamine, enta = ethylenediaminetetraacetic acid. [c] Rate expressed at ml. H_2 (515 mm.) per minute; initial rate given for cupric acetate and cystine. [d] Computed on basis of reduction to hydroquinone or cuprous acetate. [e] Prior to the "break point." [f] 80 minutes after the "break point."

Discussion

It is reasonable to assume that en, enta and cystine coördinate with cuprous acetate, displacing either acetate ion or quinoline from the coördination sphere. The ability of cuprous acetate to catalyze quinone hydrogenation is decreased by the addition of en and enta. This may be associated with a steric interference with the substrate quinone, rather than with prevention of hydrogen activation, since the reduction of the catalyst to metallic copper can still proceed in the presence of en. The fact that added chelating agent has a smaller effect on cupric acetate reduction than on quinone reduction may also be interpreted as evidence for a specific effect with quinone. It is also possible, however, that the chelating agent combines preferentially with the cupric ion, leaving the cuprous acetate catalyst relatively unaffected.

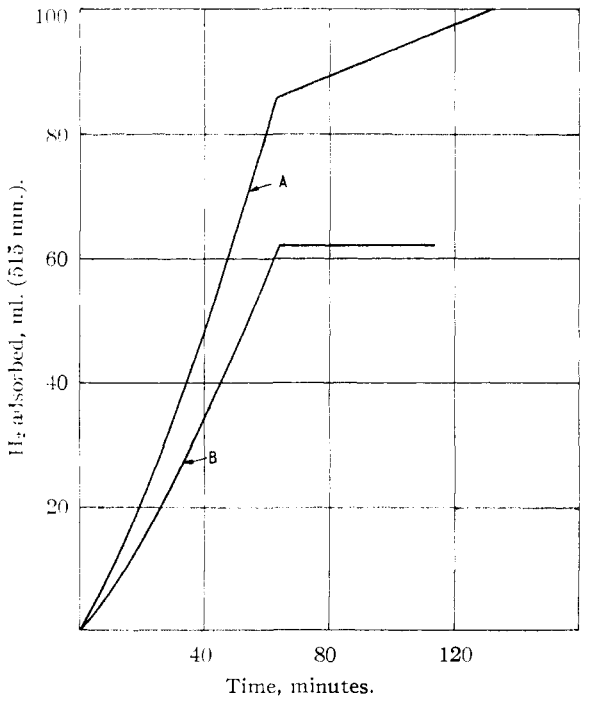

Fig. 1.—Hydrogenation of cupric acetate and benzoquinone; effect of enta: curve A, 2.0 millimoles of benzoquinone, 2.1 millimoles of cupric acetate, 2.0 millimoles of cuprous acetate, 40 ml. of quinoline, 100°; curve B, 0.5 millimole of enta, 2.0 millimoles of benzoquinone, 2.0 millimoles of cupric acetate, 3.2 millimoles of cuprous acetate, 40 ml. quinoline, 100°.

The reduction of cuprous acetate to metallic copper is an interesting reaction in relation to the general problem of how hydrogen is activated in this system. The question may be raised whether this reduction occurs by the same mechanism as that involved in the catalyzed quinone reduction,[2] and whether a dimeric catalyst molecule is also necessary here in order to dissociate a hydrogen molecule. The cystine-catalyzed reduction of cuprous acetate proceeded only to 55% completion (Table I, run 466). Over this range, the data were equally well fit by a rate law which was first-order either in cuprous acetate monomer, or in cuprous acetate dimer, a dimerization constant of 11.2 $mole^{-1}$ l. being assumed.[2] The kinetics thus do not permit a clear statement concerning mechanism for this case. It should also be noted that the mechanism previously given for the catalyzed quinone hydrogenation[2] does not explain the catalysis of cuprous acetate reduction by en, cystine or reduced quinone.

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