mixture was heated on a steam-bath for 1 hour and filtered while hot. Cooling of the filtrate caused the separation of 0.4 g. of a brownish crystalline solid which melted, after being washed with water, at 224–229°. Recrystallized from ethanol, the product was colorless and melted at 236–237° alone or when mixed with a sample of the material obtained by method A.

1,6-Diduryl-2,5-dimesityl-1,3,5-hexatriene-1,6-diol Diacetate.—A solution of 0.5 g. of the diol in 25 ml. of acetic anhydride was heated under reflux for 90 minutes. Cooling caused the separation of 0.49 g. of white needles, m.p. 252–255°. The diacetate was purified by recrystallization from glacial acetic acid; m.p. 275°.

Anal. Calcd. for $C_{48}H_{56}O_4$: C, 82.71; H, 8.09. Found: C, 82.41; H, 8.26.

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The Polarographic Behavior of Methyl Vinyl Ketone and Methyl Vinyl Sulfone[1]

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Most α,β-unsaturated carbonyl compounds exhibit, on polarographic reduction, two waves which have been considered to be due to the reduction of the enol form of the compound (*p*H dependent) followed by the reduction of the double bond (*p*H independent).[2] If the corresponding α,β-unsaturated sulfone exhibited similar polarographic behavior, the reduction could plausibly be expected to proceed through a similar mechanism involving the enol form if it is assumed that this is the current picture of the reduction of α,β-unsaturated carbonyl compounds. In order for the sulfone to form the enol, the sulfur octet would have to enlarge to hold ten electrons. This expansion of the sulfur octet has been the subject[3] of much controversy. Thus, it seemed of interest to examine the polarographic behavior of an α,β-unsaturated sulfone and the corresponding α,β-unsaturated ketone.

The two compounds selected for investigation were methyl vinyl sulfone and methyl vinyl ketone. Only the ketone has been reported as being polarographically reducible.[4] Only one wave was observed at −1.43 v. *vs.* S.C.E. in 0.1 *M* potassium chloride solution.

Experimental

Apparatus.—All polarograms were recorded with a Sargent Polarograph Model XXI. The linearity of the potential dial was checked by means of a Leeds and Northrup Potentiometer. Half-wave potentials were read directly from the chart and were calculated to be accurate within 15 millivolts. Corning marine barometer tubing was used for the capillary which had a value of 1.51 mg.$^{2/3}$ sec.$^{1/6}$ for the capillary constant at open circuit in 0.5 *M* potassium chloride at 25°. The water-jacketed, H-type cell[5] with attached saturated calomel electrode, was maintained at 25 ± 0.2° by circulating water through the jacket from an external constant temperature bath. The *p*H of all solutions were measured with a Beckman Model G *p*H Meter.

Materials.—The methyl vinyl ketone was obtained from E. I. du Pont de Nemours and Co. as 85% azeotrope with water having about 0.5% acetic acid and 0.1% hydroquinone present. Since neither of these compounds is reduced at the dropping mercury electrode, the ketone solution was used without further purification. The methyl vinyl sulfone was prepared by the method of Price[6] and after careful purification had the following physical constants; b.p. 110° (18 mm.) (literature value[6] b.p. 115–117° (19 mm.)) and $n^{22}D$ 1.4262. Appropriate quantities of the organic compounds were dissolved in 95% ethanol and an aliquot diluted with aqueous buffer to give a final solution 0.5 m*M* in reducible species and 10% in ethanol. The buffer was 0.1 *M* with respect to buffering constituents (acetic, boric and phosphoric acids with various amounts of 1 *M* sodium hydroxide in order to cover the *p*H range 2 to 12) and 0.5 *M* with respect to potassium chloride in order that a high ionic strength (0.62 *M*) might be maintained.[7] Tank nitrogen, purified by passage through gas bubblers (one, containing concentrated sulfuric acid; a second, an alkaline solution of pyrogallol; and a third, a sample of cell solution) was bubbled through the solution in the polarographic cell for five minutes before polarographing. Polarograms were recorded over the potential range 0 to −2 volts *vs.* S.C.E. at a suitable sensitivity. The half-wave potentials were determined by the usual graphical method.

Results and Discussion

The half-wave potential *vs.* *p*H curves for both ketone and sulfone are shown in Fig. 1. It is seen that methyl vinyl ketone exhibits the polarographic behavior expected of an α,β-unsaturated carbonyl compound, *i.e.*, two waves, one *p*H dependent and one *p*H independent. Methyl vinyl sulfone, on the other hand, exhibits only one wave which is *p*H independent indicating that the double bond is the only group present that is polarographically reducible in the potential range available. This lack of reduction of the sulfone group may be explained by the inability of the sulfone group to form an appreciable concentration of conjugate acid (see following paragraph).

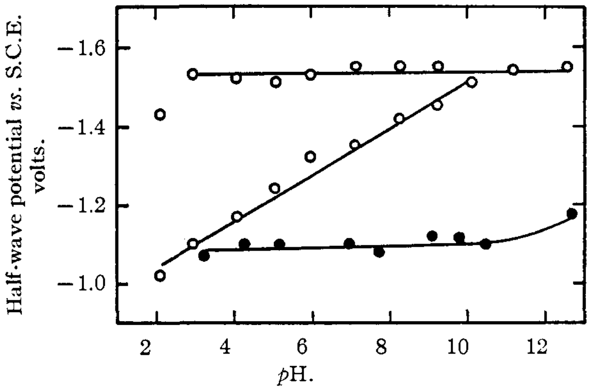

Fig. 1.—Half-wave potential *vs.* *p*H curves for methyl vinyl sulfone (closed circles) and methyl vinyl ketone (open circles).

Thus, another possible mechanism of the reduction of the α,β-unsaturated carbonyl group could involve, rather than the reduction of the enol form, the reduction of the conjugate acid of the keto form I which would be expected to be *p*H dependent.

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[1] Abstracted from the thesis of C. W. Johnson, submitted in partial fulfillment of the requirements of the degree Master of Science in Chemistry, June, 1952.

[2] S. Wawzonek, *Anal. Chem.*, **21**, 62 (1949).

[3] For an excellent discussion of this question see H. P. Koch and W. E. Moffitt, *Trans. Faraday Soc.*, **47**, 7 (1951). In particular it is demonstrated that due to the geometry of the orbitals in linear α,β-unsaturated sulfone systems less expansion or less interaction of the electrons of the double bond and of the sulfone group is probable than in the cyclic α,β-unsaturated sulfone systems that are present in substituted thiophene-1-dioxides.

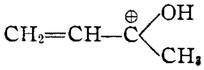
[4] E. I. Fulmer, J. J. Kolfenbach and L. A. Underkofler, *Ind. Eng. Chem., Anal. Ed.*, **16**, 469 (1944).

[5] J. C. Komyathy, F. Malloy and P. J. Elving, *Anal. Chem.*, **24**, 431 (1952).

[6] C. C. Price and J. Zomlefer, THIS JOURNAL, **72**, 14 (1950).

[7] P. J. Elving, J. C. Komyathy, R. E. VanAtta, C. S. Tang and I. Rosenthal, *Anal. Chem.*, **23**, 1218 (1951).

The second wave would again result from the reduction of the double bond. Thus, the nonreduction of the sulfone group could be attributed to the difficulty of forming appreciable concentrations of the conjugate acid of the sulfone (II) due to the inability of structures such as II-b to contribute proportionately to the resonance hybrid. It is, of course, possible that the conjugate acid reduces



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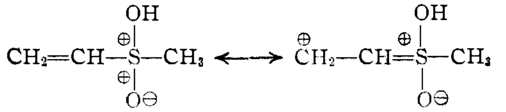

IIa IIb

with great difficulty and that this accounts for the difference in ease of reduction. The absence of acid catalysis in halogen addition to methyl vinyl sulfone[8] can also be ascribed to the absence of conjugation involving structures such as IIb.

[8] I. R. C. McDonald, R. M. Milburn and P. W. Robertson, *J. Chem. Soc.*, 2836 (1950).

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Low Temperature Heat Capacities of Inorganic Solids. XIII. Heat Capacity of Lithium Borohydride[1]

BY NATHAN C. HALLETT AND HERRICK L. JOHNSTON

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Introduction

The only measurements of thermodynamic interest thus far reported on lithium borohydride are the heats of formation by Davis, Mason and Stegeman.[2] As part of the Cryogenic Laboratory program of measuring the thermodynamic properties of the boron hydrides and of the metallo borohydrides the heat capacity of solid lithium borohydride has been measured from 15 to 303°K.

Apparatus and Material

The heat capacity measurements were made in calorimeter No. 1, one of a group of seven calorimeters for the measurements of the heat capacity of solid materials. This calorimeter has been described in an earlier paper.[3]

The sample of lithium borohydride was obtained through the courtesy of the General Electric Research Laboratory at a reported purity of approximately 95%. The sample was purified and analyzed by the method of Davis, Mason and Stegeman,[2] except that all handling of the sample, including purifying, filling, sealing and emptying the calorimeter was done under an anhydrous nitrogen atmosphere in a dry-box. The resulting purity was found to be 99.7%. The calorimeter contained 9.9290 g. (0.4556 mole) of lithium borohydride.

Experimental Results

The experimental heat capacity data, summarized in Table I, follow a normal S-shaped curve.

TABLE I

MOLAR HEAT CAPACITY OF LITHIUM BOROHYDRIDE ($LiBH_4$)

Mol. wt. 21.79; 0.4556 mole

Mean T, °K.	C_p, cal./mole/deg.	Mean T, °K.	C_p, cal./mole/deg.
15.72	0.1781	225.36	15.65
19.37	.2484	231.97	15.96
21.76	.3369	238.75	16.30
23.64	.3981	244.35	16.59
25.39	.4723	249.53	16.74
27.40	.5546	250.48	16.83
30.71	.7642	254.66	17.02
34.28	.9532	255.97	17.12
38.04	1.226	259.50	17.28
42.41	1.585	260.63	17.353
46.88	2.027	262.14	17.45
51.67	2.374	264.87	17.63
56.55	2.854	266.59	17.70
61.06	3.310	267.60	17.73
62.08	3.384	269.11	17.94
67.12	3.892	270.41	17.96
72.79	4.390	272.45	18.07
78.65	5.072	272.82	18.21
84.98	5.755	272.96	18.24
86.23	5.894	274.47	18.24
92.82	6.516	277.65	18.44
99.93	7.168	278.32	18.50
107.76	7.895	278.71	18.53
115.93	8.618	280.25	18.75
124.42	9.324	283.77	18.87
132.35	9.975	284.15	18.90
140.02	10.49	284.76	18.95
147.33	11.08	288.74	19.10
155.32	11.631	288.75	19.12
164.09	12.21	289.20	19.18
172.37	12.67	293.43	19.48
180.82	13.13	294.27	19.50
188.84	13.63	296.95	19.62
196.83	14.06	298.50	19.74
204.66	14.50	299.20	19.74
212.05	14.91	299.47	19.80
218.86	15.28	302.88	20.02

Table II gives the heat capacity and derived thermodynamic functions for lithium borohydride at selected integral values of the temperature.

TABLE II

THERMODYNAMIC FUNCTIONS FOR LITHIUM BOROHYDRIDE ($LiBH_4$)

Temp., °K.	C_p, cal./mole/deg.	S^0, cal./mole/deg.	$(H^0_0 - H^0)/T$, cal./mole/deg.	$-(F^0 - H^0_0)/T$, cal./mole/deg.
15	0.152	0.0874	0.0515	0.0359
25	0.451	0.225	.144	.0811
50	2.235	1.013	.692	.322
75	4.709	2.373	1.606	.766
100	7.188	4.077	2.700	1.376
125	9.371	5.919	3.820	2.099
150	11.246	7.799	4.906	2.892
175	12.832	9.655	5.929	3.726
200	14.250	11.462	6.881	4.581
225	15.617	13.221	7.777	5.444
250	16.802	14.930	8.622	6.308
275	18.254	16.595	9.428	7.168
298.16	19.733	18.131	10.226	7.904
300	19.847	18.252	10.230	8.022

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(1) This work was suported in part by the Office of Naval Research under contract with The Ohio State University Research Foundation.

(2) W. Davis, L. Mason and G. Stegeman, Thermal Properties of Some Hydrides, Univ. of Pittsburgh, ONR Contract Number N6ORI-43, Task Order No. 1, Technical Report, Dec 1, 1948.

(3) H. L. Johnston and E. C. Kerr, THIS JOURNAL, **72**, 4733 (1950).