carried until no further hydrogen was absorbed. The hydrogen uptake was corrected for catalyst absorption.

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Some Keto-Enol Equilibria in the Gas Phase

BY ROBERT SCHRECK[1]

Conant and Thompson[2] have measured the positions of the keto-enol equilibria for several 1,3-dicarbonyl compounds in the gas phase. In the work reported below, similar data have been obtained for the two further tautomeric systems: ethyl cyclopentanone-2-carboxylate and ethyl cyclohexanone-2-carboxylate. For purposes of comparison, ethyl acetoacetate has also been reexamined in the gas phase, and all three of the esters named have been studied in the liquid state.

Procedures

The samples of the esters were equilibrated in the vapor phase in the way that was developed by Conant and Thompson.[2] The only significant departures from the original procedure were, in fact, (1) that the condensate from the slow low-pressure distillation was collected in a tube cooled with liquid nitrogen (−196°), rather in one cooled with solid carbon dioxide (−80°); and (2) that the contents of the distilling flask were kept thoroughly mixed by stirring with a glass-enclosed nail, which was magnetically rotated at 300 r. p. m., rather than by shaking. That equilibrium was indeed attained was shown, as in the work of Conant and Thompson, by the fact that successive fractions of the distillate showed essentially identical properties.

The "low-enol" ethyl acetoacetate that had been equilibrated in the liquid state was analyzed by the familiar indirect bromine titration of K. H. Meyer, with the use of diisobutylene for the removal of the excess bromine. The "high-enol" ethyl acetoacetate that had been equilibrated in the gas phase was analyzed by comparing its measured refractive index $n^{20}\text{D}$ with a curve drawn to represent Beyaert's empirically determined relation between refractive index and composition.[3] The two cyclic esters, equilibrated both in the liquid state and in the gas phase, were analyzed by Meyer's direct bromine titration.

Results

The results of the measurements described above are collected in the accompanying table. It will be noted that small, but significant, discrepancies exist between the values found in this investigation and those reported in the earlier literature. These discrepancies presumably indicate the order of magnitudes of the unavoidable uncertainties that must be expected in such work. It will also be noted that the abnormally high enol content of ethyl cyclohexanone-2-carboxylate in the liquid state is retained, and in fact increased in the gas phase.

TABLE I

KETO-ENOL EQUILIBRIA IN THREE β-KETOESTERS

Ester	State	No. of runs[a]	% enol at 25°[b] Range	Average value	Standard dev.	Lit.
Ethyl acetoacetate	Liquid	3	7.38–7.41	7.39	0.01	7.4[c,d]
	Gas	9	46.6–51.6	49.3	1.6	45.3–46.9[e]
Ethyl cyclopentanone-2-carboxylate	Liquid	3	4.55–4.65	4.60	0.04	4.45[c,f]
	Gas	7	26.7–28.3	27.5	0.5	....
Ethyl cyclohexanone-2-carboxylate	Liquid	4	72.9–74.5	73.7	0.6	76.0[c,f]
	Gas	7	89.9–91.7	90.6	0.6	....

[a] A number of runs which were made while the procedures were being perfected are omitted from this table. [b] In the measurements reported in this paper, the equilibria with the liquid esters were attained at room temperature, which was considered to be sufficiently close to 25°; the equilibria with the gaseous esters were attained by keeping the distilling flask in an oil thermostat held at 25 ± 0.2°. [c] At 20°. [d] K. H. Meyer, *Ber.*, 45, 2843 (1912). [e] J. B. Conant and A. F. Thompson, Jr., THIS JOURNAL, 54, 4039 (1932). [f] W. Dieckmann, *Ber.*, 55, 2470 (1922).

Materials

Ethyl acetoacetate (Carbide and Carbon Chemicals Corporation, technical grade) was washed with distilled water, dried over an excess of anhydrous copper sulfate, dried further over Drierite, and then distilled at 12–15 mm. pressure. The observed refractive index, $n^{20}\text{D}$ 1.4191, agreed with Beyaert's value[3] for the equilibrium ester (7.4% enol).

Ethyl cyclopentanone-2-carboxylate and ethyl cyclohexanone-2-carboxylate were prepared by the procedures described in "Organic Syntheses."[4] At equilibrium, the refractive index $n^{20}\text{D}$ of the liquid cyclopentanone derivative, 1.4519, was in complete agreement with the value reported by Van Rysselberghe.[5] On the other hand, that of the cyclohexanone derivative, 1.4779, was in poor agreement with value of 1.4750 for $n^{17.5}\text{D}$, reported by Feofilaktov[6]; for this reason, special pains were taken to ensure that the compound was pure and that equilibrium had actually been reached. The freshly distilled ("high-enol") material with $n^{20}\text{D}$ equal to 1.4819 was allowed to

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[1] This paper was written on the basis of the laboratory notebooks and incompleted Master's thesis which were left by Robert Schreck at his untimely death.—G. W. WHELAND.

[2] J. B. Conant and A. F. Thompson, Jr., THIS JOURNAL, **54**, 4039 (1932).

[3] M. Beyaert, *Natuurw. Tijdschr.*, **18**, 209 (1936).

[4] "Organic Syntheses," Coll. Volume 2, A. H. Blatt, editor, John Wiley and Sons, Inc., New York, N. Y., 1943, pp. 116ff and 531ff, respectively.

[5] M. van Rysselberghe, *Bull. sci. acad. roy. Belg.*, [5] **11**, 171 (1926).

[6] V. V. Feofilaktov, *Bull. acad. sci. U. R. S. S. Classe sci. chim.* 521 (1941); *C. A.*, **37**, 2347 (1943).

stand with small amounts of barium hydroxide or of tetraethylammonium hydroxide, or with soft-glass beads; in every case, the refractive index decreased to the value of 1.4779, cited above, and then remained constant for at least three weeks.

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X-Ray Powder Patterns of Boron Coated Mo and W Filaments

BY ST. V. NARAY SZABO AND CHARLES W. TOBIAS[1]

In 1945 we conducted a series of experiments on the preparation of pure crystalline boron. Our object was to obtain boron in such a form that X-ray studies concerning the crystallographic structure would be possible. After the beginning of World War II, scientific information, especially from the United States, was unobtainable. This is why important papers, such as the extensive study of Laubengayer, *et al.*,[2] were unknown to us. In most respects the above-mentioned authors attained more significant results than we did. Nevertheless, the techniques we used and the data obtained might eventually be of some use in further studies.

1. **Preparation of Pure Boron.**—A modification of van Arkel's method for thermal dissociation of boron tribromide[3,4] seemed to us the most promising. The regulation of boron tribromide vapor stream in van Arkel's original apparatus (Fig. 1) was effected by separate temperature control of two boron tribromide containers, making it difficult to attain a steady state. Also the quantity of boron tribromide necessary to fill such an apparatus would have been too large. Having only a few grams of boron tribromide at our disposal, we used a much smaller cylinder, 3 cm. in diameter and 4 cm. high, and only one boron tribromide container was connected to it. The apparatus used for the deposition of pure boron is shown in Fig. 2.

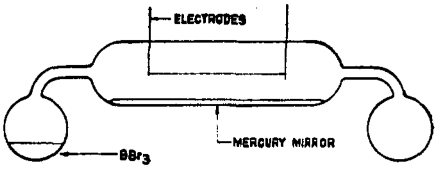

Fig. 1.

Boron tribromide was prepared by using Meyer and Zappner's modified Moissan method.[5] After purification by distillation the boron tribromide was sealed in small glass capsules and stored, when not used immediately. In preparation for the thermal decomposition, the apparatus already containing the boron tribromide was cooled under −50°, flushed with hydrogen and then evacuated to 1–1.5 mm. By controlling the temperature of the boron tribromide container, the density of boron tribromide vapor in the reaction space was fixed by the vapor pressure of boron tribromide at the given liquid temperature. The bromine liberated at the filament was instantaneously bound by the mercury mirror at the bottom of the cylinder. To keep the mercury surface fresh, small

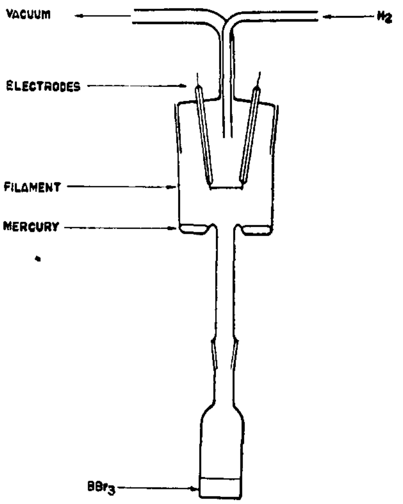

Fig. 2.

TABLE I

POWDER PATTERN OF THE "GRAPHITIC" TYPE BORON

B on W filament	I_{est}	B on Mo filament Sin² θ	I_{est}	Calculated	Miller's index
0.0326	7	0.0325	7	0.0324	200
.0362	9	.0356	7	.0360	002
408	3	412	4	414	201
445	3	440	3	441	102
732	2	734	2	729, 738	300, 221
888	8	880	6	891	311
0.1020	8	0.1020	10	0.1008	222
1100	2	1120	2	1089, 1134	302, 203
1210	2	1205	2	1215	213
1310	7	1320	9	1296	400
1462	2	1470	2	1458, 1467	330 ,223, 411
1650	6	1620	4	1620	420
?		1780	2	1764	204
1980	3	1995	3	1980	422
2160	2	2150	2	2169	304
?		2400	1	2412	115
2550	1	2540	2	2574	205
2630	6	2620	5	2592, 2655	440, 215
2780	2	2780	2	2817	414
2850	1	2850	1	2835	433
?		2930	4	2916	513
3110	4	3080	2	3087	611
3260	4	3260	4	3276	006
3340	3	3350	4	3357	612
3550	3	3560	4	3546	514, 405

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[2] A. H. Laubengayer, D. T. Hurd, A. E. Newkirk and J. L. Hoard, THIS JOURNAL, **65**, 1924 (1943).

[3] v. Arkel, *Metallwirtschaft*, **XIII**, 23, 29 (1934).

[4] v. Arkel, "Reine Metalle," Springer Verlag, 1939.

[5] Gmelin-Kraut, "Handbuch der anorganischen Chemie."