[CONTRIBUTION FROM THE LOS ALAMOS SCIENTIFIC LABORATORY]

The Vapor Pressures of Hydrogen, Deuterium and Tritium up to Three Atmospheres[1]

BY E. R. GRILLY

Introduction

Recently 15 cc. (S.T.P.) of tritium from the Li^6 + neutron reaction became available for vapor pressure measurements. Although the development of its purification is incomplete, it is felt to be sufficient to yield fair accuracy in the measurements, which covered a range of 14–29°K. Data were also obtained for hydrogen and deuterium in the ranges 14–24.5° and 14–27.8°, respectively, parts of which have been previously measured.[2–9] The present paper presents data which allow a self-consistent comparison in vapor pressures of the three isotopes[10] up to 2100 mm. and which can be compared with the tritium values calculated by Hammel[11] from De Boer's theory of corresponding states, in which quantum effects are taken into account.

The apparatus, designed essentially for small volume, consisted of: (a) sample bulb; (b) Toepler pump; (c) condensing tube; (d) manometer; (e) thermometer; (f) bath. Apiezon-greased stopcocks were used successfully at all points.[12] The Toepler pump was designed to vary the pressure in the condensing tube from 0 to 3 atm. The Pyrex condensing tube,[13] was 1 mm. i.d., 2 mm. o.d. in the upper region and 2 mm. i.d., 3.5 mm. o.d. in the short lower part where the gas was condensed. The manometer system was made by connecting one side of a calibrated 0–100 mm. Hg differential gage (made by Wallace and Tiernan Co.) to the condensing tube and the other side to a main manometer and pressure-adjusting nitrogen. This arrangement provided a small, rather constant volume for the tritium yet allowed coverage of a large pressure range. For the main manometer two types were used; (1) a mercury manometer for the region 0–1400 mm. Hg; (2) a 0–30 p.s.i. Bourdon gage for 1400–2100 mm. Hg. The latter was made by U. S. Gauge Co., had a 16″ diameter scale, had a guaranteed accuracy of 0.5%, and agreed to 1 mm. with two mercury manometers in occasional calibrations. Next to the condensing tube was the special platinum resistance thermometer, enclosed in a platinum capsule, made by Leeds and Northrup Co., and calibrated by the National Bureau of Standards for the region 10–90°K. The baths used were liquid hydrogen (14 to 24.5°) and liquid neon (24.6 to 29°) kept at constant temperature by automatic pressure regulation and constant stirring.[14] The Dewar was surrounded with liquid nitrogen and had a sliding seal at the top which facilitated checking vapor pressure as a function of tube immersion depth.

Procedure.—Gas was slowly admitted to the condensing tube in the constant-temperature bath, and pressures in the tube were noted. Condensation was indicated by constant pressure (in the absence of impurity). The hydrogen and deuterium used were distilled "99.9% pure" commercial grades. Hydrogen in the tritium sample was removed by R. M. Potter of this Laboratory, using Hertz pumps, to less than 0.5%, as determined by two different mass spectrometers. A typical analysis showed 0.07% H_2 and 0.73% HT. To retard the picking up of hydrogen from stopcock grease and adsorbed water, the tritium was stored as uranium tritide(UT_3) at room temperature where the decomposition pressure is $\sim 10^{-5}$ mm. Hg. Before each run, the decay product He^3 was pumped off and the tritide heated to 400°C. to give gaseous tritium.

Each gas had its purity checked by noting at several temperatures that the vapor pressures were constant during a tenfold change in amount of condensate. Thus it is felt that even in the case of tritium, where the hydrogen concentration in the bulk gas might double during the course of a run, the gas actually in contact with liquid was much purer.

Results and Discussion

From 14 to 20°K. the hydrogen vapor pressure data fit (within 0.01°) the equation

$$\log P \text{ (mm. Hg)} = 4.66687 - 44.9569/T + 0.020537\,T \quad (1)$$

which has been derived at Natl. Bur. Stds.[2] from a variety of data. From 19.5° to 24.5°K. the results are given in Table I and can be expressed by the equation[15]

$$\log P \text{ (mm.)} = 5.5567 - 54.650/T + 10.9 \times 10^{-4}\,(T - 22)^2 \quad (2)$$

In the table the measurements are compared with results from equation (2) and with results of other investigations.

In Table II are the deuterium data and their deviations from the derived equations

$$\text{solid: } \log P = 6.2100 - 77.077/T + 28.8 \times 10^{-4}\,(T - 16.5)^2 \quad (3)$$

$$\text{liquid: } \log P = 5.8404 - 70.044/T + 4.59 \times 10^{-4}\,(T - 23)^2 \quad (4)$$

In Fig. 1 the equations are compared with results of other workers after putting their hydrogen vapor pressures into Eq. (1) to get temperatures onto a common scale. Also, the reported data of Brickwedde, *et al.*,[6] were found to be in error due to

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[1] This paper is based on work performed under University of California contract with the Atomic Energy Commission.

[2] F. G. Brickwedde and R. B. Scott, unpublished but cited in the compilation of properties of hydrogen by H. W. Woolley, R. B. Scott and F. G. Brickwedde, *J. Research Natl. Bur. Standards*, **41**, 379–475 (1948): H_2, 14.0 to 20.4°K. (54 to 760 mm. Hg).

[3] F. Henning and J. Otto, *Physik. Z.*, **37**, 633 (1936): H_2, 14.0 to 20.4°K.

[4] W. H. Keesom, A. Bijl and H. v. d. Horst, *Comm. Leiden*, **217a** (1931); H_2, 14.5 to 20.4°K.

[5] P. G. Cath and H. Kamerlingh Onnes, *ibid.*, **152a** (1917): H_2, 24.5 to 33.2°K. (3 to 13 atm.).

[6] F. G. Brickwedde, R. B. Scott and H. S. Taylor, *J. Research Natl. Bur. Standards*, **15**, 463 (1935) RP841; *J. Chem. Phys.*, **3**, 653 (1935): D_2, 17.4 to 20.4°K. (40 to 252 mm. Hg).

[7] R. B. Scott, F. C. Brickwedde, H. C. Urey and M. H. Wahl, *ibid.*, **2**, 454 (1934): D_2, 15.2–20.3°K. (14 to 252 mm. Hg).

[8] G. N. Lewis and W. T. Hanson, Jr., THIS JOURNAL, **56**, 1687 (1934): D_2, 15.3 to 20.4°K. (17 to 256 mm. Hg).

[9] H. J. Hoge and J. W. Lassiter (of Natl. Bur. Stds.) by private communications give preliminary data, subject to minor adjustments, on normal D_2 at 21°; 20° equil. D_2, 18 to 38.3°K. (0.13 to 16.5 atm.).

[10] For each, the ortho–para ratio is assumed to be the high-temperature or "normal" value, 2:1 for deuterium and 3:1 for hydrogen and tritium, since all known catalysts were absent and the vapor pressures were independent of time within the range of 1 to 30 minutes after condensation.

[11] E. F. Hammel, *J. Chem. Phys.*, **18**, 228 (1950).

[12] Some "freezing" of stopcocks has been encountered elsewhere. This is apparently due to presence of oxygen in the tritium.

[13] The first tube used was of stainless steel, 0.028″ i.d., 0.042″ o.d. This gave essentially the same vapor pressures as did the Pyrex.

[14] Mechanical stirring was abandoned in favor of convection induced by one or more of these heat leaks to the bottom of the bath: (1) thermometer leads, (2) electrical heater, (3) external lamp. Results were the same, but mechanical stirring was too awkward.

[15] This four-constant equation seems superior to the usual three-constant equation of the form $\log P = A + B/T + CT$ in that its third term is much smaller. This fact simplifies calculations, especially when going from P to T.

TABLE I

VAPOR PRESSURES OF LIQUID NORMAL HYDROGEN, 19.5-24.5°K.

T, °K.	P, this res.[a] (mm.)	Dev. from Eq., %	P, others (mm.)	$T_{\text{this res.}} - T_{\text{others}}$ (× 10³)	Sources of other data
19.560	587.8	−0.02	589.0	6	Equation of Natl. Bur. Stds.[2]
20.092	694.7	.25	694.9	1	
21.323	986.6	− .04	991.8	19	Extrapolation of Natl. Bur. Stds. eq.[2]
22.047	1196.8	.02	1200.9	14	
22.803	1445.9	− .16	1457.7	35	
23.412	1675.0	− .14	1688.2	38	
23.941	1897.4	.07	1908.7	30	
24.445	2125.7	− .02	2137.0	29	
24.445	2125.7		2127.9[b]	6	Cath and K. Onnes[5]

[a] Date, May 12, 1950. [b] Extrapolated from 24.59°K.

transcribing incorrectly; the present comparison uses their correct data.[16] Above 21°K. the only data available for comparison are those by Hoge and Lassiter[9] on 20°K. equilibrium deuterium which might be expected to have vapor pressures greater than those of the normal variety by an approximately constant factor.

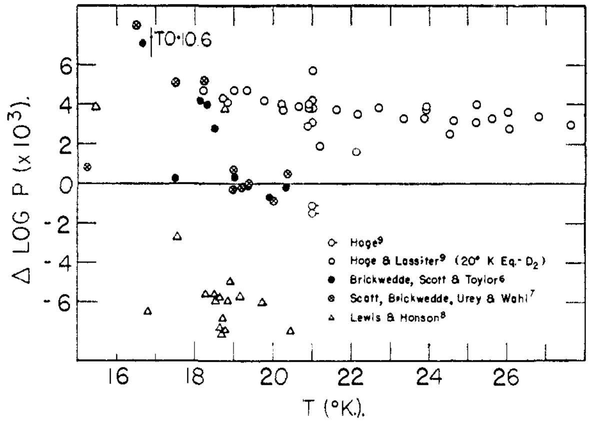

Fig. 1.—Comparison of deuterium vapor pressures: $\Delta \log P = \log P$ (measured by others) $- \log P$ (equations of present paper).

Table III gives the tritium data along with their deviations from the derived equations

$$\text{solid: } \log P = 6.4773 - 88.002/T \qquad (5)$$

$$\text{liquid: } \log P = 6.0334 - 78.925/T + 2.0 \times 10^{-4}(T - 25)^2 \qquad (6)$$

The large deviations around the triple point are somewhat surprising, but similar results had been obtained with less accurate preliminary measurements. Table IV gives a comparison of the present data with those calculated by Hammel.[11]

TABLE II

VAPOR PRESSURES OF NORMAL DEUTERIUM

Date	T (°K.)	P, mm.	Dev. from eq., %
		Solid	
1	13.966	5.0	−2.3
4	13.966	5.2	1.4
4	14.946	11.8	2.7
1	15.072	12.2	−3.6
1	15.861	22.5	0.11
4	15.915	23.5	.71
4	16.548	35.5	− .46
1	16.525	37.7	.57
4	16.980	47.1	.34
1	17.031	48.3	− .28
4	17.426	61.6	.05
1	17.453	62.7	.21
4	17.791	76.1	− .25
1	17.824	77.8	.07
2	17.953	83.9	.23
1	18.195	96.0	.02
2	18.226	97.9	.23
4	18.251	98.7	− .34
2	18.472	112.0	.11
4	18.539	116.6	.48
2	18.668	124.3	− .10
1	18.687	125.4	− .23
2	18.710	127.3	.02
		Liquid	
2	18.873	137.1	.10
4	19.042	147.4	− .18
1	19.045	148.3	.28
2	19.570	185.4	.32
1	19.584	186.4	.32
4	19.587	185.6	− .28
1	19.590	186.5	.10
1	20.095	228.1	− .13
1	20.565	272.4	− .44
1	20.985	320.2	.21
1	21.456	376.4	− .32
1	21.833	429.5	.05
1	22.289	499.3	.07
1	22.778	582.4	− .02
1	23.244	673.2	.25
1	23.668	759.1	− .21
1	24.107	858.3	− .41
1	24.487	958.4	.11
3	24.562	978.2	.14
3	25.087	1121.1	− .18
3	25.493	1247.1	.02
3	25.872	1371.5	.07
3	26.304	1524.2	.11
3	26.304	1525.1	.18
3	26.649	1652.1	− .05
3	26.974	1781.7	− .02
3	27.239	1892.8	− .02
3	27.489	2002.6	.00
3	27.778	2133.3	− .10

Dates of measurement: (1) 2/3/50, liquid hydrogen bath, 14.0–24.5°K.; (2) 2/8/50, liquid hydrogen bath, 18.0–19.6°K.; (3) 2/9/50, liquid neon bath, 24.6–27.8°K.; (4) 6/3/50, liquid hydrogen bath, 14.0–19.6°K.

Heats of sublimation and vaporization were calculated from $\Delta H = T\Delta V \mathrm{d}P/\mathrm{d}T$. The vapor pressure relations were taken from Eqs. (2), (3), (4), (5) and (6) and the Natl. Bur. Stds. equation for solid hydrogen: $\log P = 4.56488 - 47.2059/T + 0.03939\ T$. In all cases V_{gas} was calculated from the equation of state[2]

$$V = RT/P - RV_0A/PVT^{1/2}$$

where V_0 = 22.428 liter and A has been determined as a function of temperature for hydrogen above 14° and for deuterium above 23°. The A values used in the computations were taken as constant =

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(16) Instead of $P(D_2) = 39.8$ at $P(H_2) = 278.3$, their results should read: $P(D_2) = 62.8$ at $P(H_2) = 278.3$ and $P(D_2) = 39.8$ at $P(H_2) = 206.1$ (all mm. Hg); by private communication.

TABLE III

VAPOR PRESSURES OF NORMAL TRITIUM

Date	T (°K.)	P(mm. Hg)	Dev. from eq., %
		Solid	
2	13.968	1.5	−0.23
2	15.274	5.4	3.8
2	16.122	10.2	−2.3
2	17.314	24.2	−2.5
1	18.054	40.2	0.28
2	18.214	43.5	−1.7
1	18.534	53.9	0.55
2	18.952	68.5	0.39
1	19.023	71.1	0.14
1	19.400	87.3	−0.02
2	19.556	94.8	− .11
1	19.746	105.1	.23
2	20.020	120.9	.18
1	20.216	133.4	.21
2	20.547	158.7	1.4
		Liquid	
1	20.647	163.7	−0.14
2	20.985	188.6	− .02
2	21.637	245.1	.32
2	22.032	283.8	.05
2	22.431	329.3	.34
2	22.776	370.5	− .09
2	23.181	425.9	− .02
2	23.557	483.2	.16
2	23.941	545.8	.00
2	24.337	618.2	.14
3	24.632	675.3	.04
3	25.182	792.0	− .25
3	25.700	917.3	.00
3	26.367	1096.5	− .09
3	27.207	1356.0	− .25
3	27.929	1617.9	− .05
3	28.586	1884.2	.00
3	29.191	2152.9	− .05

Dates of measurement: (1) 11/14/50, liquid hydrogen bath, 18.0-20.6°; (2) 11/15/50, liquid hydrogen bath, 14.0-24.3°; (3) 12/15/50, liquid neon bath, 24.6-29.2°.

TABLE IV

EXPERIMENTAL AND CALCULATED VALUES FOR VAPOR PRESSURES AND TRIPLE POINT OF TRITIUM

T (°K.)	$P_{\text{exp.}}$	$P_{\text{calcd.}}$ (mm.)
14.3	2.0	1.5
17.1	21.2	15.4
20.2	131	95
22.2	301	234
26.0	995	867
27.9	1603	1544

n.b.p.: 25.04° (exp.); 25.57° (calcd.). Triple point: 20.62°, 162.0 mm. (exp.); 21.65°, 188 mm. (calcd.).

0.71°K.$^{3/2}$ for deuterium and tritium. The results are given in Table V. For comparison, measurements on hydrogen[17] give

$$\Delta H_v(20.39°) = 215.8 \text{ cal./mole}; \ \Delta H_v(13.96°) = 217.8; \ \Delta H_f(13.96°) = 28.0; \ \Delta H_s(13.96°) = 217.8 + 28.0 = 245.8$$

Measurements on deuterium[18] give:

$$\Delta H_v(19.70°) = 302.3 \text{ and } \Delta H_f(18.72°) = 47.0, \text{ totaling } \Delta H_s \sim 349$$

Table V also serves as a summary of thermal properties connected with vapor pressures for all three isotopes.

TABLE V

SOME THERMAL PROPERTIES OF THE HYDROGEN ISOTOPES

	n-H_2	n-D_2	n-T_2
Triple point temperature, °K.	13.96	18.73	20.62
Triple point pressure, mm.	54.0	128.6	162.0
Normal boiling point, °K.	20.39	23.67	25.04
Heat of sublimation at triple pt., cal./mole	247	364	393
Heat of vaporization at n.b.p., cal./mole	216	293	333

Figure 2 gives log P *vs.* $1/T$ plots of the present data.

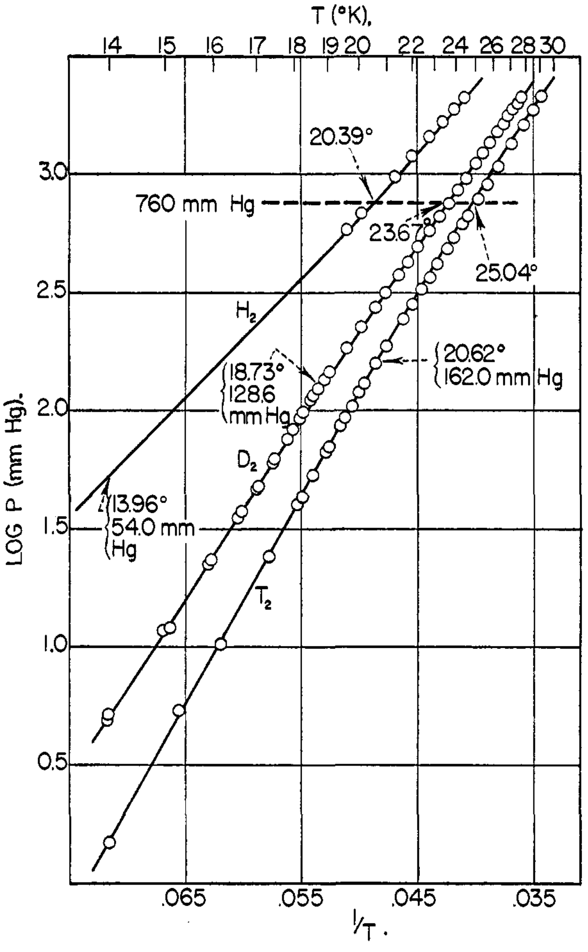

Fig. 2.—Vapor pressures of the hydrogen isotopes. For H_2 below 20°, the curve is from Eq. (1). Triple point values are noted at slope discontinuities.

It is difficult to settle on one variable which will indicate reliability over a wide range of vapor pressure data. Pressures are readable to approximately 0.1 mm. which alone means large fractional or logarithmic errors at low pressures. At high pressures, temperature and impurity uncertainties set the limits of reliability. If each of these is constant over a range of measurement, an average of the fractional deviations in pressure from the derived equations should be significant. Such approximate average deviations amount to: 0.1% in pressure or 0.004° in temperature for hydrogen;

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(17) F. Simon and F. Lange, *Z. Physik*, **15**, 312 (1923).

(18) K. Clusius and E. Bartholome, *Z. physik. Chem.*, **B30**, 237 (1935).

0.2% or 0.005° for deuterium; 0.3% or 0.007° for tritium. Other sources of error, namely, the radioactive heat (amounting to 8.63 × 10^{-5} watt/std. cc. of gas[19]) and possible rapid equilibration between ortho and para forms of tritium seem to be inapplicable in the present measurements.

Summary

1. The vapor pressures of hydrogen, deuterium and tritium have been measured up to three atmospheres.

2. Triple points and heats of vaporization and of sublimation have been derived from the vapor pressures.

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[19] G. H. Jenks, J. A. Ghormley and F. H. Sweeton, *Phys. Rev.*, **76**, 701 (1949).

NOTES

Simple Preparation of Optically Active Secondary Alcohols[1]

BY AKSEL A. BOTHNER-BY

It has been well established that reduction of some classes of organic compounds by lithium aluminum hydride is accomplished by transfer of a hydride ion to an electrophilic center of the molecule being reduced.[2] The nature of the ions or neutral molecules donating the hydride ion has not been determined, but a reasonable hypothesis is that in the reduction of a ketone, the forms $Al(OR)_mH_n$ are present, where –OR represents the alkoxyl group derived from the ketone, and *m* and *n* are small integers. If this is the case, partial reaction of lithium aluminum hydride with *d*-camphor would give a species capable of asymmetric reduction of ketones. Similar asymmetric reductions have been reported by Vavon and co-workers,[3] Mosher and LaCombe,[4] and Doering.[5] Reductions of methyl ethyl ketone and pinacolone with lithium aluminum hydride–*d*-camphor have been performed. Table I shows for three runs the ketone reduced, the number of moles of lithium aluminum hydride, *d*-camphor and ketone used, and the boiling point and optical activity of the alcohol obtained.

TABLE I

Ketone reduced	Moles			Alcohol	
	$LiAlH_4$	*d*-Camphor	Ketone	B.p., °C.	$[\alpha]^{25}D$
Methyl ethyl	0.100	0.200	0.200	99.5–100	+2.50
Pinacolone	.118	.118	.354	118–120	+0.04
Pinacolone	.111	.222	.222	118–120	+0.82

Experimental

The reductions were in each case similar to the following:

Optically Active *s*-Butyl Alcohol.—To a stirred solution of 3.80 g. of lithium aluminum hydride in 300 ml. of ether under nitrogen, was added dropwise a solution of 30.0 g. of *d*-camphor in 50 ml. of ether. Addition required one-half hour. A mixture of 15.0 ml. of methyl ethyl ketone and 50 ml. of ether was then dropped in over one-half hour, followed immediately by 100 ml. of 17% HCl. Stirring was continued until two clear layers were present. The layers were separated, and the ether layer, after drying with calcium chloride pellets, was fractionated through a small Vigreux column. The *d*-isoborneol solidified in the pot. The distillate was refractionated twice to obtain 10.0 g. of *s*-butyl alcohol; $n^{25}D$ 1.3975, b.p. 97–100°, d^{20}_4 0.8084.

A subsequent fractionation through a 40-plate column packed with glass helices gave alcohol having $n^{25}D$ 1.3974, b.p. 99.5–100.0°, d^{20}_4 0.8081, $[\alpha]^{25}D$ +2.50°.

BROOKHAVEN NATIONAL LABORATORY
UPTON, LONG ISLAND, N. Y.
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[1] Work done under the auspices of the Atomic Energy Commission.

[2] L. W. Trevoy and W. G. Brown, THIS JOURNAL, **71**, 1675 (1949).

[3] (a) Vavon and Angelo, *Compt. rend.*, **224**, 1435 (1947); (b) Vavon, Riviere and Angelo, *ibid.*, **222**, 959 (1946).

[4] Mosher and LaCombe, THIS JOURNAL, **72**, 3994 (1950).

[5] W. von E. Doering, *ibid.*, **72**, 631 (1950).

$\Delta^{5,7}$-Steroids. IV.[1] 7-Dehydrocholesteryl Methyl Ether

BY SEYMOUR BERNSTEIN AND KARL J. SAX

In this note we wish to record the preparation in a pure state of 7-dehydrocholesteryl methyl ether from cholesteryl methyl ether *via* the NBS[2] method.[1,3] This compound has been described previously only in the patent literature,[4] and was prepared by a modified Windaus method.[5]

Cholesteryl methyl ether in petroleum ether was brominated with NBS, and the intermediate bromo compound (not isolated) was dehydrobrominated with *s*-collidine in xylene in the usual manner[1] of this Laboratory. This gave a mixture of the desired $\Delta^{5,7}$-ether and the expected by-product, $\Delta^{4,6}$-cholestadienyl methyl ether. Recrystallization from acetone gave the pure $\Delta^{5,7}$-ether, m. p. 123–125°. This m. p. is in contrast to that given by Rosenberg and Turnbull, Jr.,[4] m. p. 109–111°. Our product was further characterized by optical rotatory power, ultraviolet and infrared absorption spectra (Fig. 1, cholesteryl methyl ether included for comparison purposes).

The material in the mother liquors was triangularly recrystallized from acetone and acetone–methanol. This gave an additional quantity of $\Delta^{5,7}$-ether, and a constant melting mixture of

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[1] Paper I, Bernstein, Sax and SubbaRow, *J. Org. Chem.*, **13**, 837 (1948); Paper II, Bernstein, Binovi, Dorfman, Sax and SubbaRow, *ibid.*, **14**, 433 (1949); Paper III, Bernstein, Oleson, Ritter and Sax, THIS JOURNAL, **71**, 2576 (1949).

[2] NBS = N-bromosuccinimide.

[3] Bide and Wilkinson, British Patent 614,194 (Dec. 10, 1948); *C. A.*, **43**, 5810 (1949), have claimed to have prepared several 7-dehydrocholesteryl ethers, *e.g.*, ethyl ether, by the NBS method, but this work is not definitive.

[4] Rosenberg and Turnbull, Jr., U. S. Patent 2,386,636 (Oct. 9, 1945).

[5] Windaus, Lettré and Schenck, *Ann.*, **520**, 98 (1935); Haslewood, *J. Chem. Soc.*, 224 (1938).