done, no study has as yet been reported in which all of the monomethyl-1,2-benzanthracenes and/or -benzo(c)phenanthrenes have been tested under reasonably constant conditions. The difficulties inherent in the attempt to assign the degree of carcinogenic potency to any hydrocarbon are well summarized in the Introduction to the latest survey on carcinogenic activity.[5] Fortunately, work which will provide some of the necessary data[6] on the methyl-1,2-benzanthracenes and -benzo(c)-phenanthrenes is now in progress in the laboratories of E. von Haam (Ohio State University) and I. Berenblum (Weizmann Institute).

Despite this present lack of complete quantitative data on the carcinogenic properties of these hydrocarbons, it is fairly well established that among the monomethyl-1,2-benzanthracenes, the 10-methyl is the most active cancer producing agent, the 5- and 9-methyl derivatives are slightly less active, while the 1′-derivative is comparatively inactive.[5,6]

From this qualitative information it is apparent that there is no correlation between carcinogenic activity of the hydrocarbon and the dissociation constant (or free energy of formation) of its TNF complex. For example, the TNF complex of the 5-methyl derivative is less stable than that of the 10-methyl while the 9-methyl complex is more stable. Furthermore, relatively inactive carcinogens form complexes which are about as stable as the 10- (*e.g.*, the 8-methyl), more stable (*e.g.*, the 7-methyl), or even less stable (*e.g.*, the 1′- and 2′-methyl). There are not enough data on the carcinogenic activity in the benzo(c)phenanthrene series to make any comparisons.

Recently the bathochromic shifts in the ultraviolet absorption of 1,2-benzanthracene produced by the substitution of a methyl group for each of the twelve hydrogens have been determined.[7] A comparison of the observed shifts with the conjugating power (calculated both by the molecular orbital and valence bond methods) of the hydrocarbons was made. The stabilities of the hydrocarbon–TNF complexes given in Table I show no correlation with either the bathochromic shifts or the conjugating power of the hydrocarbon.

Orchin[8] has discussed steric effects in the formation of complexes of tetracyclic compounds. He states that "although substitution of a methyl group on the hydrocarbon usually enhances the ease of formation and stability of the picrate, if the methyl group is located where steric interference (methyl, hydrogen overlap) is possible, complex formation is often made difficult or the complex forms in other than a 1:1 ratio." With the methyl-1,2-benzanthracenes such steric interference is possible in the case of the 9-methyl (overlap with 1′-hydrogen) and 1′-methyl (overlap with the 9-hydrogen); in 1-methylbenzo(c)phenanthrene considerable overlap with the 1′-hydrogen is possible. Orchin used the melting point of the picrate as a criterion of its stability,[9] concluding that the 9-methyl-1,2-benzanthracene picrate, because of its low melting point (see Table II), is unstable; he noted that the 1′-methyl was not a 1:1 complex and that the 1-methylbenzo(c)phenanthrene complex did not form.

Since the TNF compounds with the methyl-1,2-benzanthracenes and -benzophenanthrenes are all formed in a ratio of 1:1, an evaluation of the general applicability of the melting point as a criterion of complex stability is afforded. While these compounds may be arranged into groups which melt fairly closely and have comparable stability, there are notable exceptions. The 9-methyl complex is the lowest melting (209°) of the 1,2-benzanthracenes, but is the second most stable; the 1′-methyl is the second highest melting, but is the next to the least stable.

The effect of the methyl, hydrogen overlap on the stability of the TNF complexes is of interest. The 1′-methyl-1,2-benzanthracene complex is, indeed, relatively unstable, but the 9-methyl complex is the second most stable. As would be expected from steric considerations, the complex compound with 1-methylbenzo(c)phenanthrene is the most unstable of its series.

We are presently engaged in determining the rate of reaction of the hydrocarbons of the 1,2-benzanthracene series with maleic anhydride and the equilibrium constants for these reactions.

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(5) "Survey of Compounds which Have Been Tested for Carcinogenic Activity," 2nd Ed., Federal Security Agency, Public Health Service Publication No. 149, U. S. Government Printing Office, Washington, D. C., 1951.

(6) *Ibid.*, 1st Ed. On p. 9 J. L. Hartwell says, "The most obvious need, as is shown by the table, is for more complete investigation of compounds already studied in a preliminary fashion."

(7) G. M. Badger, R. S. Pierce and R. Pettit, *J. Chem. Soc.*, 1112 (1952).

(8) M. Orchin, *J. Org. Chem.*, **16**, 1165 (1951).

(9) See also C. Shinomiya, *Bull. Chem. Soc. Japan*, **15**, 92, 137, 281 (1940).

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Densities and Freezing Points of Sodium Permanganate Solutions

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In the use of strong solutions of sodium permanganate it became necessary to know the densities and phase diagram for the system sodium permanganate–water. The temperature at which a solid phase appears was determined for solutions from 0 to 96 weight per cent. sodium permanganate. The salt received for this work analyzed 88 weight per cent. and when dried *in vacuo* at 100° the analysis rose to 98.5% sodium permanganate. Further drying did not improve the purity. All compositions are given on the weight basis and corrected to the $NaMnO_4$ and water content only. The 1.5% is considered inert and as playing no part on freezing point curves. Solutions were made up by mixing weighed amounts of salt and water and titrations against standard sodium oxalate were used to check the concentration. The freezing points composition curves were obtained by recording the cooling curves for various concentrations of sodium permanganate in the standard way; *i.e.*, the solutions were mechanically stirred during cooling and seed crystals added where any tendency to undercool was apparent. The recording was accomplished with a four junction copper–constantan thermocouple and a Leeds and Northrup recording potentiometer. The thermocouple was calibrated over the range used against fixed points using a reference junction at 0°. A smooth curve was obtained over the range.

Difficulty was experienced in obtaining cooling curves for solutions above 89.4 weight per cent. sodium permanganate and reproducible freezing points were not obtained for the eutectic between the monohydrate and anhydrous material.

In Table I, the temperatures are given at which a solid phase appears for a given percentage of sodium permanganate. The compositions of solid phases were calculated from the composition of the solutions at the freezing point. For concentrations below 41.4% the solid phase is ice; between 41.4 and 75.2% the solid phase is sodium permanganate trihydrate with a melting point at 36.0°. Between 75.2 and about 91% the solid phase is monohydrate with a melting point at 68.7°. Above about 89.4% the data are rendered somewhat questionable due to decomposition of the sample; however, the points obtained may indicate the possible existence of hydrate containing 1/2 molecule of water. No freezing point could be determined above 96% due to decomposition. The phase diagram is shown in Fig. 1. The doubtful part of the diagram is shown by a dotted line. Each solution used is indicated with a different type point.

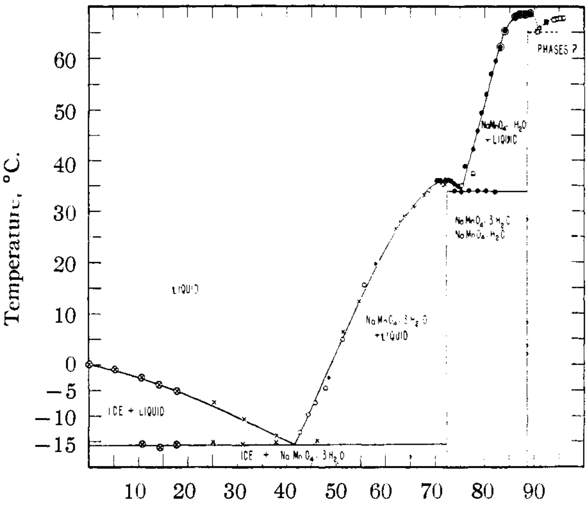
TABLE I

$NaMnO_4$,[a] Wt. %	F.p., °C.	$NaMnO_4$, Wt. %	F.p., °C.	$NaMnO_4$, Wt. %	F.p., °C.
0	0	36	−13.2	70	35.3
2	− 0.5	38	−14.1	72	36.0
4	− 0.9	40	−15.0	74	35.3
6	− 1.4	41.4	−15.8E	75	34.0
8	− 2.0	42	−14.7	75.2	33.7E
10	− 2.5	44	−10.7	76.0	36.4
12	− 3.2	46	− 6.2	78.0	45.6
14	− 3.8	48	− 2.0	80	51.5
16	− 4.6	50	+ 2.25	82	59.0
18	− 5.3	52	6.6	83	62.5
20	− 6.1	54	10.8	84	65.2
22	− 7.0	56	15.0	86	67.7
24	− 7.7	58	18.9	88	68.7
26	− 8.5	60	22.5	90	68.0?
28	− 9.5	62	25.8	90.7	66.2E?
30	−10.3	64	30.7	92	66.5?
32	−11.2	66	31.3	94	67.6?
34	−12.2	68	33.7	96	67.6?

[a] The sodium permanganate content is based on the titratable permanganate and water only.

Density.—The densities of sodium permanganate solutions were determined by the use of water-calibrated 50-cc. dilatometers.

Five different concentrations based on the weight of titratable sodium permanganate were used. These were put in the dilatometers by means of a fine capillary tube. Both the solution and dilatometer were kept at 0° during the operation in order to keep the opaque solutions from getting on the upper portion of the calibrated tube. The solutions were apt to cling to the sides of the tube and thereby make it difficult to read the volume as well as lead to error in the volume read. The dilatometers were then placed in the thermostat set at a given temperature and allowed to come to equilibrium. This was ascertained by observing the volume in the capillary. A cathetometer was used to obtain readings on the height in the capillary tubes. The volumes were easily read to 0.0001 cc.



Concentration of $NaMnO_4$ in weight per cent.

Fig. 1.

The volumes were determined at 1.35, 13.0, 25.3 and 37.45° for each of the five solutions by use of five dilatometers. In order to be sure the temperatures were constant in each case readings were taken until a constant volume was obtained. To be sure that there was no loss in weight of the solutions during the determinations, they were weighed at frequent intervals. No loss occurred.

The determined densities are given in Table II.

TABLE II

DENSITY OF $NAMNO_4$ SOLUTIONS (G./CC.)

$NaMnO_4$, Wt. %	Temperature, °C. 1.35	13.00	25.30	37.45
5.32	1.0404	1.0390	1.0361	1.0319
10.58	1.0843	1.0817	1.0776	1.0725
14.05	1.1148	1.1110	1.1062	1.1005
17.62	1.1471	1.1429	1.1371	1.1310
25.60	1.2243	1.2180	1.2110	1.2034

The measurements and values given herein have become available for publication though declassification of part of a program of study pursued in 1939. While more complete data would be desirable those available appear worthy of recording in the published literature.

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