

PHYSICAL CONSTANTS OF DIOLEFINS						
Compound	B. p. (760 mm.), °C.	F. p. (m. p.), °C.	F. range, °C.	d_{20}^4	n_D^{20}	Source
1,6-Heptadiene	90.01	-129.35	0.16	0.7142	1.4142	Pres. res.
	89.77134	1.4142	Frank ⁶
" <i>cis-cis</i> -2,7- Nonadiene"	151.0	glass	..	.7582	1.4368	Pres. res.
<i>trans-trans</i> -2,7- Nonadiene (by sodium alone)	150.3	-72.46	0.08	.7499	1.4358	
<i>trans-trans</i> -2,7- Nonadiene (by sodium and (NH ₄) ₂ SO ₄)	150.5	-76.2	55	.7515	1.4360	

III. Catalytic Hydrogenation.—2,7-Nonadiyne was treated with hydrogen in presence of nickel as described under dialkylacetylenes. Since it would be hard to separate a diene from the corresponding enyne, exactly one equivalent of hydrogen was supplied. The last 10% was absorbed but slowly. The purified product gave indications of being a mixture and no freezing point could be determined, but its other constants varied in the direction expected from those of the pure *trans-trans* compound. The *cis* configuration probably predominated in this diene but did not exclude the *trans*.

Summary

Monoalkylacetylenes were quantitatively reduced to the corresponding olefins by reaction with sodium in liquid ammonia containing am-

(6) Frank, Dissertation, The Ohio State University, 1938.

monium sulfate; the use of soluble ammonium salts caused inefficient reduction.

Dialkylacetylenes were quantitatively reduced (in liquid ammonia) by sodium alone to pure *trans* olefins; ammonium salts led to mixtures of geometric isomers presumably due to the intervention of nascent hydrogen. Catalytic hydrogenation of dialkylacetylenes produced olefins in which the *cis* configuration predominated.

Diacetylenes were similarly treated. 1,6-Heptadiyne was reduced to 1,6-heptadiene by sodium and ammonium sulfate. 2,7-Nonadiyne was reduced by sodium to pure *trans-trans*-2,7-nonadiene, while catalytic hydrogenation yielded a substance which was obviously a mixture.

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RECEIVED MAY 22, 1943

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY, HAVERFORD COLLEGE]

The Molal Depression Constant for Camphor

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Probably no solvent has been more used by organic chemists as a means of finding the molecular weights of newly-prepared substances by the cryoscopic method than camphor. Hence the establishment of the numerical value of the molal depression constant for this solvent is a matter of considerable importance. Of the several values extant in the literature the one which has been most generally accepted is that of Rast, 39.7.¹ Of the values in disagreement with that obtained by Rast and others² the outstanding ones are those of Jounieaux, 49.5,³ Efremov, 48.7,⁴ and Durand, 49.7.⁵ The calculations of Jounieaux have been shown to be

- (1) Rast, *Ber.*, **55**, 3727 (1922).
- (2) Smith and Young, *J. Biol. Chem.*, **75**, 289 (1927); LeFèvre and Tidemann, *J. Chem. Soc.*, **107**, 1729 (1931).
- (3) Jounieaux, *Bull. soc. chim.*, **11**, 546 (1912).
- (4) Efremov, *Bull. acad. scie. Russ.*, 765 (1919).
- (5) Durand, *Bull. soc. chim.*, **57**, 67 (1937).

unreliable,⁶ but the values of the latter two still stand. Bohme and Schneider⁷ have given, without experimental data, several isolated values which suggested to the authors of this paper that the cryoscopic constant for camphor might vary with the concentration. It was to test this hypothesis that the present investigation was undertaken. Such a variation has been noted by Pirsch in the case of camphene dibromide as solvent.⁸ Using various solutes, Pirsch obtained values for the molal depression constant which, although quite discordant for solutions of less than about 8 mole-per cent. solute, showed a regular decrease between 9 and 21 mole-per cent. from about 116 to about 45.

- (6) LeFèvre and Tidemann, *Nature*, **127**, 972 (1931).
- (7) Bohme and Schneider, *Angew. Chem.*, **52**, 58 (1939).
- (8) Pirsch, *Ber.*, **69**, 1229 (1932).

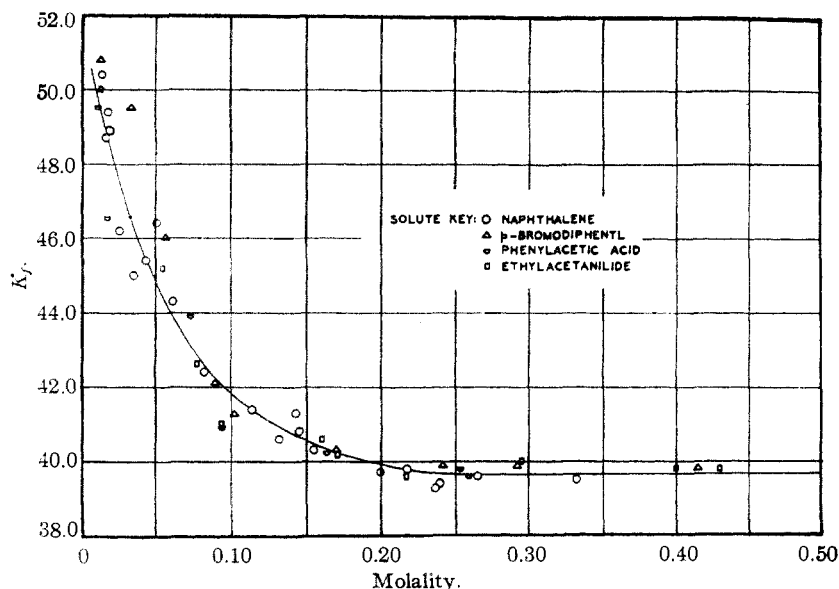


Fig. 1.

Procedure.—The freezing point was determined by a modified Rast procedure. Suitable quantities of *d*-camphor and the solute were weighed into small stoppered test-tubes and carefully melted in an oil-bath.

TABLE I

ΔT_f AND K_f VALUES FOR CAMPHOR WITH DIFFERENT SOLUTES AT VARIOUS CONCENTRATIONS

Molality	ΔT_f	K_f	Molality	ΔT_f	K_f
Naphthalene			<i>p</i> -Bromodiphenyl		
0.014	0.70°C.	50.4	0.013	0.65°C.	50.8
.016	.80	48.7	.034	1.70	49.5
.017	.85	49.4	.057	2.60	46.0
.018	.90	48.9	.089	3.75	42.1
.027	1.25	46.2	.101	4.15	41.3
.036	1.60	45.0	.170	6.85	40.3
.044	2.00	45.4	.242	9.65	39.9
.051	2.35	46.4	.293	11.70	39.9
.061	2.70	44.3	.415	16.50	39.8
.083	3.50	42.4			
.114	4.70	41.4			
.132	5.35	40.6			
.143	5.90	41.3			
.146	5.95	40.8			
.155	6.25	40.3	0.012	0.60	49.5
.200	7.95	39.7	.018	0.85	46.5
.218	8.70	39.8	.073	3.20	43.9
.237	9.30	39.4	.093	3.80	40.9
.240	9.45	39.6	.163	6.55	40.2
.266	10.55	39.5	.253	10.00	39.8
.332	13.15	39.8	.260	10.30	39.6
.556	22.15		.554	21.80	39.4
Ethylacetanilide					
0.013	0.65	50.0	0.171	6.90	40.2
.054	2.45	45.2	.217	8.60	39.6
.078	3.30	42.6	.295	11.80	40.0
.094	3.85	41.0	.400	15.95	39.8
.160	6.50	40.6	.429	17.05	39.8

After a thorough mixing, the solution was cooled and the solidified mass ground in a mortar. It was then introduced into a thin-walled melting-point tube and the end carefully sealed off. The capillary container was then immersed in the oil of the melting point apparatus and the temperature slowly raised; the temperature at which the last crystal disappeared was taken as the freezing point of the solution. The freezing points were determined using an apparatus similar to that described by Hershberg⁹ with an internal heating coil. By carefully controlling the potential across the heating coil by means of a Variac the temperature could easily be maintained constant within 0.05° at about 175°. The maintenance of the temperature virtu-

ally constant over a long period was essential to safeguard against superheating or supercooling.

For early experiments the solvent camphor was purified by sublimation and had a freezing point of 178.45°. This was used, for example, in the determinations with naphthalene and *p*-bromodiphenyl as solutes. Further investigation showed that the results using unsublimed camphor were quite satisfactory and this camphor with a freezing point of 178.60° was used for the experiments with phenylacetic acid and ethylacetanilide as solutes.

The freezing-point depressions, ΔT_f , obtained for solutions of these solutes in various concentrations in camphor and the corresponding values of the molal depression constant, are given in Table I; the values of K_f for camphor are plotted against the molal concentrations of the same solutes in Fig. 1.

Discussion of Results

The results plotted in Fig. 1 show clearly that in solutions above 0.2 *m* the value for K_f for camphor remains constant at about 39.7, but in solutions of lower concentration the values of the constant increase with decreasing concentration, approaching a maximum of about 50. Thus Rast's value was confirmed but only for concentrations above 0.2 *m*; an examination of his data showed that he had, in fact, worked with concentrations between 0.2 and 0.6 *m*. Durand's value of the constant was found to have been deduced from measurements with concentrations between 0.06 and 0.2 *m*. The relatively large experimental error when using very dilute solutions made it impracticable, by the method used by the authors, to extrapolate to a significant value

(9) Hershberg, *Ind. Eng. Chem., Anal. Ed.*, **8**, 312 (1936).

for K_f at infinite dilution. In any case, such a value would be of no practical importance in the determination of molecular weights.

To verify the results obtained by the Rast method cooling curves were obtained for pure *d*-camphor and for solutions of naphthalene in camphor. Comparatively large quantities of camphor (29 g.) were used. The camphor or the solution was melted in a small cylindrical Dewar flask by an electrically heated platinum coil immersed in it and its freezing point was found by the conventional time-temperature curve method. In order to obtain a sharp break it was found necessary to insulate the Dewar flask by suitable packing. The freezing point of the pure *d*-camphor found by this method, 178.4°, checked closely with that obtained by the Rast method, 178.6°. Naphthalene solutions of molal concentrations 0.031, 0.11 and 0.21, gave freezing point depressions of 1.25, 4.45 and 8.55°, respectively. The values of K_f calculated from these depressions are 46.4, 41.3 and 39.7, corresponding closely with the values for the same concentrations as determined by the Rast method. The results obtained with the Rast method are probably more accurate.

From these results it is obvious that in order to determine the molecular weight of an *unknown* substance with camphor as solvent, care must be taken to use solutions of concentrations sufficiently high to justify the use of the constant 39.7. A lower limit in concentration of 0.2 *m* is indicated. In order to ascertain what constitutes a 0.2 *m* solution a rough determination of

the molecular weight must first be carried out.

The change in K_f over the low concentration range presents a paradoxical situation. The expression relating K_f with the heat of fusion, L_f , of the solvent, *viz.*

$$K_f = RT^2/1000L_f$$

is presumed to apply most accurately to solutions of *low* concentrations. But applying this equation to the experimentally determined heat of fusion of camphor, 1630 ± 60 cal. × mole⁻¹, Frandsen¹⁰ found K_f to be 37.7 ± 1.4 deg., mole⁻¹, kg., a value very close to that found experimentally for the *higher* concentration range.

No satisfactory explanation for the variation of K_f with concentration has been conceived. Pirsch⁸ suggests the possibility of cleavage of the solute but the close concordance of the K_f values for different solutes at low concentrations militates against this view. The results would also be explained by assuming a partial association of the solvent in low solute concentrations.

Summary

It has been shown that the uncertainty regarding the value of the molal depression constant for camphor has been caused by the fact that the constant changes with changing concentration. The value of the constant 39.7 deg., mole⁻¹, kg. holds for concentrations above 0.2 *m*; below this concentration the constant increases with decreasing concentration to a maximum of about 50.

(10) Frandsen, *B. S. Jour. of Res.*, **7**, 477 (1931).

HAVERFORD, PA.

RECEIVED DECEMBER 30, 1942

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 937]

An Electron Diffraction Study of Hydrogen Peroxide and Hydrazine

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Introduction

We undertook the investigation of the hydrogen peroxide and hydrazine molecules in order to determine the lengths of the oxygen-oxygen and nitrogen-nitrogen covalent single bonds which they contain, and so directly to fix the values of the corresponding single-bond covalent radii which had previously been estimated only by indirect methods.² Because of the relatively

low scattering power of hydrogen atoms nothing could be learned about the other interatomic distances in hydrogen peroxide, and only rough values were found for hydrazine. We wanted also to study hydroxylamine, but its instability was even more troublesome than that of hydrogen peroxide and we gave up our efforts to photograph it after a few unsuccessful attempts.

The covalent radii of oxygen and nitrogen (and

(1) Present address: Laval University, Quebec, Canada.

(2) (a) L. Pauling and M. L. Huggins, *Z. Krist.*, **87**, 205 (1934);

(b) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y.