sults have been cited among ethylene reactions by Egloff[2] but apparently have never had experimental confirmation.

As such a reaction would be of great interest in both synthetic work and theoretical discussions, we have attempted to produce it, but our efforts have been uniformly unsuccessful. Impure ethylene does yield a white solid when passed over or bubbled through molten sodium at 150°, but if the ethylene be purified by bubbling it through one or two test-tubes of the metal at this temperature, it does not react at all with more sodium. Such tarnishing of the metal as does then occur is due to air and moisture adsorbed on glass surfaces in the apparatus, for it can be diminished greatly by flaming the container tube and connections before use. The white solid that was formed in the scrubber tubes by the impure ethylene did not have the reactivity which would be expected of an organometallic compound of sodium. We were likewise unable to find any evidence of polymerization of the ethylene. Indeed, according to Walker's own data, little or no ethylene was consumed by polymerization or reaction with sodium, and the purity of the gas actually increased during the reaction.

(2) Egloff, "The Reactions of Pure Hydrocarbons," Reinhold Publishing Corp., New York, N. Y., 1937, p. 288.

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Refraction Data on Liquid C3-Hydrocarbons

BY ARISTID V. GROSSE AND CARL B. LINN

One of us[1] recently has described the adaptation of the Abbé refractometer to low temperature measurements.

We have now completed measurements of the refractive indices for the D-line, at low temperatures, of all known C3-hydrocarbons with the exception of cyclopropene.[2] (Very little is known about this hydrocarbon and none of its physical properties have ever been measured.) In order to obtain the molecular refractions we have determined, with Mr. R. C. Wackher, the still unknown densities of cyclopropane and allene.

In the following table the n_D and d_4^t (corrected to vacuum) of propane, propene, cyclopropane, propyne (allylene) and propadiene (allene) are recorded for the temperature range of −20 to −80° and also at their respective normal boiling points.

(1) A. V. Grosse, THIS JOURNAL, 59, 2739 (1937).
(2) N. J. Demjanow and M. Dojarenko, Ber., 56, 2200 (1923).

The C3-hydrocarbons show wide differences in their indices. These may be used advantageously for analytical purposes since binary mixtures of these hydrocarbons show with sufficient accuracy a straight line relationship. Particularly interesting cases are the propane–propene mixtures, obtained in catalytic dehydrogenation, or propyne-propadiene mixtures from isomerization studies.

The molecular refractions of these hydrocarbons are of interest since they are the lowest members of the series so far studied in the liquid state. The Lorenz–Lorentz refractions were calculated from the data of Table I for different temperatures and the values extrapolated to +20° are compared with values computed from Eisenlohr's atomic refractions in Table II. Molecular volumes are included for comparisons.

The experimental molecular refractions (extrapolated to +20°) are in as good agreement with the calculated values as can be expected in view of their large temperature coefficients. These variations with temperature are much greater than for higher molecular weight compounds, measured around room temperatures; however, from the standpoint of the theory of corresponding states this is at least partly to be expected, since the absolute position and range of our measurements cover about 20% of the total distance from absolute zero to the normal boiling point.

The only real deviation is observable in the case of cyclopropane. The difference, equalling 0.4 unit, evidently is due to the exaltation of the cyclopropane ring. This exaltation value is slightly less than the one obtained by L. Tschugajeff[3] (=0.66) on strained or substituted cyclopropane derivatives (carone, thujene, etc.).

The sources of hydrocarbons were as follows:

Propane, from the Phillips Petroleum Company, c. p. grade, over 99% pure.
Propene, from the Matheson Company, c. p. grade, over 99% pure.
Cyclopropane, from the Mallinckrodt Chemical Company, over 99% pure.
Propyne, prepared by us by treating sodium acetylide with dimethyl sulfate.[8]
Propadiene, prepared for us by Dr. R. E. Schaad from 2,3-dibromopropane and zinc.[4]

Each hydrocarbon was purified carefully by fractionation on a low temperature Podbielniak column. Five cuts were taken on the plateau

(3) L. Tschugajeff, Ber., 33, 3122 (1900).
(4) G. Gustavson and N. Demjanow, J. prakt. Chem., [2] 38, 202 (1888).

TABLE I

Temp., $t°$ °C.	n^tD					D^t_4 (vac.)				
	Propane	Propene	Cyclopropane	Propyne	Propadiene	Propane[5]	Propene[6]	Cyclopropane	Propyne[6]	Propadiene
−20	....	....	....	1.3725	....	....	....	....	0.6670	....
−30	....	....	1.3706	1.3793	1.4137	....	....	0.6769	.6791	0.6575
−40	1.3378	1.3567	1.3769	1.3863	1.4214	0.5800	0.6002	.6886	.6911	.6699
−50	1.3447	1.3640	1.3833	....	1.4291	.5915	.6132	.7002	....	.6822
−60	1.3517	1.3712	1.3897	....	1.4368	.6029	.6258	.7119	....	.6944
−70	1.3587	1.3785	1.3960	....	1.4444	.6145	.6386	.7235	....	.7004
−80	1.3657	1.3857	1.4024	....	....	.6259	.6513	.7352	....	....
@N. b. p.	1.3392	1.3623	1.3726	1.3747	1.4168	.5829	.6100	.6807	.6698	.6624
Normal b. p.	−42.2[7]	−47.8	−32.7	−23.3[8]	−34.34[8]	−42.2[7]	−47.8	−32.7	−23.3[8]	−34.34[8]

$dn_D/dt°$ and, respectively, $dD/dt°$

| −0.000698 | −0.000725 | −0.000638 | −0.000690 | −0.000768 | −0.00115 | −0.00128 | −0.00117 | −0.00120 | −0.00122 |

TABLE II

Hydrocarbon	Carbon skeleton	Mol. volume at N. b. p., cc.	Experimental molecular refractions, MR^{LL}D					Extra-polated to +20°	Calculated MR^{LL}D (at +20°)	Temp. coeff. MR^{LL}D /°C. (from −80° to −20°)
			@N. b. p.	−80°	−60°	−40°	−20°			
Propane	C—C—C	75.65	15.83	15.76	15.79	15.83	...	15.9	16.05	+0.0017
Propene	C—C=C	68.98	15.30	15.15	15.24	15.34	...	15.6	15.62	+ .0047
Cyclopropane	C△ (C—C—C ring)	61.82	14.06	13.94	13.99	14.04	14.10	14.2	(13.85)[a]	+ .0025
Propyne	C—C≡C	59.81	13.65	...	...	13.61	13.66	13.8	14.05	+ .0025
Propadiene	C=C=C	60.48	15.19	15.03	15.10	15.17	...	15.3	15.12	+ .0035

[a] $3 \times CH_2$.

corresponding to the boiling point of the pure substance. The nD of each fraction was measured and a cut whose index did not vary over 0.0002 from adjacent cuts was used for our final measurements. These were made at temperature intervals of about 10°. For all hydrocarbons studied the nD was a straight line function of temperature; the values of Table I were read off the line for even temperature intervals.

For measuring nD below −50° reduced pressure was employed on liquid propene circulating through the refractometer. By this procedure we were able to measure easily nD at as low as −75°, when using dry-ice as the cooling medium.

(5) O. Maass and C. H. Wright, THIS JOURNAL, 43, 1098 (1921).
(6) F. R. Morehouse and O. Maass, Can. J. Research, 11, 637 (1934).
(7) M. M. Hicks-Bruun and J. H. Bruun, THIS JOURNAL, 58, 810 (1936).
(8) See J. H. Vaughn, L. F. Hennion, R. R. Vogt and J. A. Nieuwland, J. Org. Chem., 2, 1 (1937).

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Two Notes on the Deamination of Glycine in the Presence of Tyrosinase and p-Cresol

BY STEPHEN S. HUBARD

When collecting data which indicate that p-cresol oxidized in the presence of tyrosinase functions reversibly in the oxidative deamination of glycine,[1] it was found that this reversibility, although considerable, is not complete. The smaller amounts of p-cresol do not take care of as much glycine as do the larger ones, although the amounts are greater than those theoretically equivalent, as discussed in the paper cited. Second, as found by others,[2] the amount of ammonia recovered is less than what corresponds to the amount of glycine deaminized. These two facts suggest that part of the oxidized p-cresol, and part of the glycine nitrogen, either as ammonia, or without being released as ammonia, are consumed in forming the intense dichroic coloration (red by reflected light, blue by transmitted light) characteristic of the digestion solutions. It seemed significant that the color of the one solution from which the theoretical amount of ammonia was recovered (1 mg. of p-cresol with 50 mg. of glycine) was green and showed no dichroism.

A few drops of dilute ammonia were added to a solution of 20 mg. of enzymically oxidized p-cresol; in a few hours the color of the solution had become greenish, similar to the one just mentioned. Formaldehyde is a possible transient end-product in the breakdown of glycine as studied here.[3] When two or three drops of formalin was added to another sample of oxidized p-cresol, a

(1) S. S. Hubard, J. Biol. Chem., 126, 489 (1938).
(2) C. E. M. Pugh and H. S. Raper, Biochem. J., 21, 1370 (1927).
(3) F. C. Happold and H. S. Raper, ibid., 19, 92 (1925).