COMMUNICATIONS TO THE EDITOR

STUDY OF SOAP MICELLES IN NON-AQUEOUS SOLVENTS USING A FLUORESCENT DYE[1]

Sir:

A number of dyes may serve as indicators for the presence of soap micelles in aqueous systems.[2] We have found rhodamine B peculiarly suited to a similar detection of soap micelles in non-aqueous solvents such as benzene, cyclohexane, cetane, and di-(2-ethylhexyl)-sebacate. This dye is slightly soluble but almost non-absorbing and non-fluorescent in benzene but fluoresces strongly upon the addition of as little as 10^{-5} mole per liter of an oil-dispersible metal soap such as the calcium or sodium salt of an arylstearic acid, a petroleum sulfonic or naphthenic acid or of an alkyl sulfonic acid.

That adsorption of the dye on the soap micelle is essential to the fluorescence observed is confirmed by this fact; the light emitted when a dilute solution containing dye and soap is illuminated with plane polarized green light is 28% polarized, whereas that from a similar concentration of the dye in methyl alcohol (with a comparable viscosity) is only 2.3% polarized. This difference is to be expected from Perrin's[3] relation for the depolarization resulting from Brownian rotation during the excited period

$$1/p = 1/p_0 + (1/p_0 - 1/3)\tau\, RT/V\eta$$

if instead of taking V equal to the hydrodynamic volume of the dye molecule one takes V to be the volume of the micelle to which the former is adsorbed. V is estimated from osmotic pressure measurements to be 14,000 cc. per "mole" in this case.[4] Taking for τ the maximum and minimum values of the average life of the excited rhodamine B molecule reported by Szymanowski[5] we calculate polarizations, p, of 20 and 26%, respectively. *These observations furnish an obvious basis for a new method of determining the average volume of soap micelles or other suitable colloids.*

If the concentration of dye in benzene is held constant while that of the soap is varied from 10^{-4} to 0 mole/liter and the fluorescence is measured under constant illumination it is found that the emission becomes undetectable at a very low but finite soap concentration, as appears in Fig. 1.

The plot of intensity against the square root of the soap concentration approximates linearity at low concentrations and permits extrapolation to determine the soap concentration at zero intensity, which we take as the critical concentration for micelle formation. For calcium xylylstearate this concentration is 1×10^{-6} mole/liter and for calcium xenylstearate it is 8×10^{-6} mole/liter.

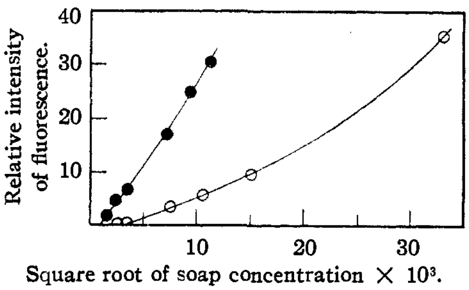

Fig. 1.—Fluorescence intensity of 2×10^{-6} molar rhodamine B in benzene as a function of soap concentration: ○, calcium xenylstearate; ●, calcium xylylstearate.

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Received September 30, 1948

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[1] The opinions or assertions contained in this communication are the authors' and are not to be construed as official or reflecting the views of the Navy Department. Not copyrighted.

[2] Corrin and Harkins, This Journal, **69**, 679 (1947).

[3] Perrin, *J. de Physique*, [VI] **7**, 390 (1926).

[4] Unpublished measurements in this Laboratory.

[5] Szymanowski, *Z. Physik*, **95**, 460 (1935).

HYDROCARBON OXIDATION INITIATED BY ATOMIC HYDROGEN[1]

Sir:

Mechanisms for the gas-phase oxidation of hydrocarbons have been proposed by many investigators. The most widely accepted of these have postulated attack on a primary C–H bond with resultant degradation to formaldehyde. Many have been based on the observation that aldehydes other than formaldehyde are absent in the products. Walsh[2] has recently reviewed these schemes and concluded that they were all unsatisfactory and has postulated that initial attack of an oxygen-containing radical should occur at tertiary in preference to secondary and secondary in preference to primary C–H bonds. Although this is to be expected, experimental evidence is largely missing, since aldehydes and ketones occurring in early stages of the oxidation are conceivably degraded to formaldehyde.

This communication reports some results of experiments in which oxidation of C_4-hydrocarbons has been initiated by atomic hydrogen. This method of oxidation, which has only been briefly previously reported for methane and acetylene by Geib and Harteck[3] supplies evidence regarding the

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[1] The work described in this paper was done in connection with Contract NOrd 7920 with the United States Naval Bureau of Ordnance, as coördinated by the Applied Physics Laboratory, The Johns Hopkins University and with Contract N6-ori-105 with the Bureau of Aeronautics and Office of Naval Research, as coördinated by Princeton University. Acknowledgement is due Dean Hugh S. Taylor, who has general supervision of this project, and Professor Robert N. Pease.

[2] A. D. Walsh, *Trans. Faraday Soc.*, **42**, 269 (1946).

[3] K. H. Geib and P. Harteck, *Z. Physik. Chem.*, **A170**, 1 (1934).

products occurring in initial stages of oxidation of paraffins and olefins. The results seem significant in that they indicate the "initial point of oxygen attack" in the gas-phase oxidation of hydrocarbons.

Experiments were carried out by mixing atom-rich hydrogen from a Wood's discharge tube with a hydrocarbon mixture. The gases reacted at 20° and products were condensed at liquid nitrogen temperature. Results (from experiments with hydrogen, hydrocarbon and oxygen in the ratio of 3:1:1; hydrogen about 60% dissociated; total pressure, 0.4 mm.; total gas velocity, 300–400 cm./sec.) in Table I show the main carbonyl products present from oxidation of C_4 hydrocarbons. Ratios of aldehyde or ketone to hydrocarbon as high as 0.20 resulted.

TABLE I

Hydrocarbon oxidized	Main carbonyl products
n-Butane	Acetaldehyde
Isobutane	Acetone, formaldehyde
1-Butene	Propionaldehyde, formaldehyde
1,3-Butadiene	Acrolein, formaldehyde, glyoxal

(Each product was definitely identified by precipitating with 2,4-dinitrophenylhydrazine, separation by fractional recrystallization and determination of melting points and mixed melting points with pure compounds.) The aldehyde or ketone first listed for each particular hydrocarbon was present in largest amount; some formaldehyde was also present in the *n*-butane products. Peroxides and other products were also present.

Insufficient evidence is available to determine the exact mechanism but the results clearly show that oxidation initially occurs at tertiary in preference to secondary and secondary in preference to primary C–H bonds. Oxidation occurs at a double bond if present.

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RECEIVED SEPTEMBER 7, 1948

RESOLUTION OF AN ALIPHATIC TERTIARY ALCOHOL

Sir:

We wish to report the partial resolution of 2,4-dimethyl-4-hexanol (I, methylethylisobutylcarbinol), apparently the first successful resolution of an aliphatic tertiary alcohol in which the hydroxyl group is attached to the asymmetric carbon atom.[1]

The racemic alcohol I, b. p. 152–153° (760 mm.); n^{18}_{D} 1.4277; n^{28}_{D} 1.4234, was synthesized according to Clarke[2] and converted to its hydrogen phthalate (II) by adding a benzene solution of the potassium salt of I to a benzene solution of phthalic anhydride according to the general procedure of Fuller and Kenyon.[3] The liquid II was purified by crystallizing its barium salt, m. p. 84–86°, from ether–pentane.

Anal. Calcd. for $C_{32}H_{42}O_8Ba \cdot H_2O$: C, 54.13; H, 6.25; Ba, 19.35. Found: C, 54.38; H, 6.54; Ba, 18.94.

The brucine salt from 139 g. of II, m. p. 139.5–140.5° (A), $[\alpha]^{28}_{\mathrm{D}}$ −7.8° [c = 6.3%],[4] crystallized in heavy prisms from acetone. After a fourteen-step systematic fractional crystallization, the brucine salt, m. p. 141–142° (B), comprising the head fraction crystallized as tight, hemispherical pellets, $[\alpha]^{26}_{\mathrm{D}}$ −4.8° [c = 9.8%].[4]

Anal. Calcd. for $C_{39}H_{48}O_8N_2$: C, 69.62; H, 7.19; N, 4.16. Found: C, 69.91, 70.32; H, 7.04, 7.15; N, 4.59, 4.11.

On regeneration the brucine salt (B) gave II, $[\alpha]^{26}_{\mathrm{D}}$ +7.3° [c = 8.0%,[4] α = 0.59°]. The curve obtained by melting mixtures of A and B showed a minimum at 136° indicating that A is a 1:1 compound of brucine −(+)-II and brucine −(−)-II.

The recovery of I was effected by adding an ethereal solution of 9.0 g. of II, $[\alpha]^{27}_{\mathrm{D}}$ +5.5° [c = 8.5%],[4] to six equivalents of ethylmagnesium bromide. The optically active I (2.0 g.) had the following properties: b. p. 78–80° (52 mm.); 152° (760 mm.); n^{18}_{D} 1.4259; $[\alpha]^{27}_{\mathrm{D}}$ −2.6° [c = 5.1%,[4] α = −0.13°].

Anal. Calcd. for $C_8H_{18}O$: C, 73.78; H, 13.93. Found: C, 73.55; H, 14.02.

During the preliminary distillation of the (−)-I there was formed some olefin, b. p. 112–115°, which showed no optical activity. A sample of II, 13.7 g., $[\alpha]^{28}_{\mathrm{D}}$ −2.7° [c = 5.1%][4], from the tail fraction gave (+)-I (2.7 g.), $[\alpha]^{28}_{\mathrm{D}}$ +1.5° [c = 5.9%,[4] α = 0.09°]; b. p. 152° (760 mm.); n^{28}_{D} 1.4234.

The infrared spectra of racemic I, partially resolved (+)-I and partially resolved (−)-I were identical in all details between 700 and 4000 wave numbers. We are indebted to Professor Ralph S. Halford and to Mr. Abraham Savitzky for these measurements.

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(1) Paolini and Divizia, *Atti accad. Lincei*, (5) **23**, 171 (1914), have claimed the partial resolution of *dl*-linalool (±1.7° instead of ±20° for the natural product) without furnishing evidence that the optical activity is due to resolved linalool rather than to a resolved impurity.

(2) Clarke, THIS JOURNAL, **30**, 1144 (1908), reported b. p. 151° (768 mm.); n^{18}_{D} 1.4286.

(3) Fuller and Kenyon, *J. Chem. Soc.*, **125**, 2304 (1924).

(4) All optical rotations were measured in 95% ethanol.

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RECEIVED NOVEMBER 1, 1948

PENICILLIN AMIDE

Sir:

In considering methods for obtaining the amide of penicillin, both the symmetrical anhydride[1] and a mixed penicillin anhydride were considered as

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(1) Carpenter, THIS JOURNAL, **70**, 2964 (1948).