on the surface establish there an equilibrium condition with the reverse processes, the association of adsorbed methyl radicals, or even more dissociated fragments with adsorbed hydrogen or deuterium atoms, yielding finally an equilibrium mixture of CH_xD_y, where $x + y = 4$. We see no reason why such dissociative processes of adsorption should not also occur with the more readily adsorbed ethylenic hydrocarbons, and contribute thereby to the exchange process. Such processes would supplement the associative type of mechanism

$$C_2H_4 + D \longrightarrow C_2H_4D \longrightarrow C_2H_3D + H$$

discussed in detail by Horiuti and Polanyi. These authors excluded the dissociative mechanism from consideration because of their observation, which agrees with our results with methane, that the exchange reaction rate is so greatly reduced when heavy water is used in place of deuterium. In our case, where a dissociative adsorption of the methane seems unavoidable, we ascribe this slower rate in presence of heavy water to the lower accessibility of the methane to the surface owing to the known stronger adsorption of the water relative to hydrogen.

Summary

1. The saturated hydrocarbon, methane, undergoes exchange with deuterium, methane-d_4 and deuterium oxide on active nickel catalysts at temperatures of 138° and higher.

2. At 184° the rate of reaction of methane with methane-d_4, deuterium and deuterium oxide decreases in the order given.

3. The activation energies of reaction with methane-d_4 and deuterium are $\sim$19 and $\sim$28 kcal., respectively.

4. The mechanism of reaction is associated with an activated, dissociative adsorption of methane on areas of surface unoccupied by hydrogen–deuterium or deuterium oxide.

PRINCETON, NEW JERSEY RECEIVED JUNE 8, 1936

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

Wetting Characteristics of Solids of Low Surface Tension such as Talc, Waxes and Resins

BY F. E. BARTELL AND H. H. ZUIDEMA

The degree of wetting can most readily be determined by measuring the angle of contact formed with the liquid and solid in question. Degree of wetting is designated as the change in free surface energy, ΔF_s, which occurs when a liquid is brought into contact with a solid (*i. e.*, $\Delta F_s = S_1 - S_{1n}$).[1] Since the free surface energy of a system is numerically equal to the surface tension, the energy change expressed in ergs per sq. cm. is numerically equal to the adhesion tension, A_{1n}, expressed in dynes per cm.

$$S_1 - S_{1n} = A_{1n} \qquad \text{(I)}$$

The adhesion tension can be evaluated in terms of the surface tension of the liquid, S_n, and the contact angle, Θ_{1n}, which the liquid forms with the solid, for, from the Young equation[2]

$$S_1 - S_{1n} = S_n \cos \Theta_{1n} \qquad \text{(II)}$$

or, for water

$$S_1 - S_{13} = S_3 \cos \Theta_{13} \qquad \text{(III)}$$

and hence

$$A_{1n} = S_n \cos \Theta_{1n} \qquad \text{(IV)}$$

or

$$A_{13} = S_3 \cos \Theta_{13} \qquad \text{(V)}$$

The adhesion tension and degree of wetting of a liquid against a solid cannot be measured directly if the contact angle is zero, but in such instances it can be determined by application of the Bartell–Osterhof[3] equation

$$A_{13} - A_{1n} = S_{n3} \cos \Theta_{1n3} \qquad \text{(VI)}$$

if the interfacial contact angle, Θ_{1n3}, is finite and measurable (as it usually is), and if the solid–water–air contact angle, Θ_{13}, is finite, so that the adhesion tension, A_{13}, can be calculated from equation (V). For solids on which water gives a zero angle, some organic liquid can usually be found which gives a finite contact angle, and equation (VI) can be used to calculate A_{13}.

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(1) The symbols used in this paper are essentially the same as have been used in recent publications from this Laboratory. S_1 = surface tension or free surface energy of a solid in air, S_n = surface tension or free surface energy of an organic liquid and S_3, the surface tension or free surface energy of water. The subscripts 1, n and 3 refer to solid, organic liquid and water phases, respectively. In this paper an interfacial contact angle between solid, organic liquid and water will be represented by Θ_{1n3}.

(2) Young, *Trans. Roy. Soc.* (London), **A95**, 65 (1805).

(3) Bartell and Osterhof, "Colloid Symposium Monograph," **5**, 113 (1927).

The Bartell–Osterhof equation (VI) can be derived mathematically by subtracting equation (II) from equation (III) and substituting in the Young[2] equation

$$S_{1n} - S_{13} = S_{n3} \cos \Theta_{1n3} \qquad \text{(VII)}$$

We thus obtain the equation

$$S_3 \cos \Theta_{13} - S_n \cos \Theta_{1n} = S_{n3} \cos \Theta_{1n3} \qquad \text{(VIII)}$$

and hence from equations (IV) and (V)

$$A_{13} - A_{1n} = S_{n3} \cos \Theta_{1n3} \qquad \text{(VI)}$$

It has been impossible, heretofore, to test the Bartell–Osterhof equation experimentally since for no solid examined could the value of each term be determined experimentally. In the present investigation, however, solids were studied which showed markedly different properties from those of solids previously studied and reported upon in papers from this Laboratory, and one of these solids, talc, has made possible the experimental testing of this equation.

The extent to which a liquid will spread over the surface of a solid is dependent upon the relative magnitudes of the three tensions involved, namely, S_1, the surface tension of the solid, S_{1n} or S_{13}, the interfacial tension solid–liquid and S_n or S_3, the surface tension of the liquid. If S_1 is greater than the sum of the other two tensions, the liquid will spread over the surface of the solid forming a continuous film. If S_1 is less than the sum of the other two tensions, spreading will be limited, a drop of the liquid will be formed which will give a definite angle of contact with the surface of the solid.

An indication of the relative surface tension values of solids is given by their relative hardness. In hard solids the atoms or ions are close together.[4–8] The force of attraction between the elementary units comprising the solids is therefore large, and the work of cohesion, and hence the surface tension, is high. In soft solids the elementary units are farther apart, and the force of attraction is much less. The work of cohesion and surface tension of soft solids is therefore small in comparison with the values for harder solids. Waxes, some resins and certain solids such as talc, pyrophyllite, graphite, etc., are very soft. Their force of cohesion, work of cohesion and hence surface tension are very low. Tests made upon some of these low surface tension solids showed that water or any organic liquid of fairly high surface tension value formed a drop, and hence a measurable contact angle upon the solid.

Experimental

The wetting characteristics of the solids studied were determined by contact angle measurements using the sessile drop method. Mack[9] has recently shown that the effect of gravity in deforming the spherical outline of sessile drops is negligible for drops of 0.5 mm. or less in diameter, except for contact angles very near 180°, and that for angles under 90° the effect is negligible even for somewhat larger drops (Figs. 1a, b and c). For a drop whose outline is the segment of a sphere, the contact angle may be calculated from the equation

$$\tan \Theta/2 = 2h/d \qquad \text{(IX)}$$

where h is the height, and d the diameter of the drop. This equation holds for acute and obtuse angles alike, and is of simple geometric derivation. Since all the drops used in this investigation were 0.5 mm. or less in diameter, equation (IX) could be used for calculating their angles of contact. Avoiding the effect of gravity by the use of small drops had the advantage that the dimensions of the drop in standard units were not required. It was necessary only to determine the ratio of h to $d/2$.

All contact angle measurements were made on freshly cleaved or freshly solidified surfaces, depending upon whether the solid was crystalline or amorphous. The liquids used were all very carefully purified and their surface tension values were in good agreement with the generally accepted values in the literature. Satisfactory results were obtained by the method if sufficient care was taken in the preparation of the surface and in placing the drop on the surface. All interfacial contact angles were measured through the water phase.

In carrying out a determination, a freshly cleaved crystal or freshly solidified surface of the solid was placed in a cell about 3 × 3 × 3 cm. with plane plate-glass sides. The solid was mounted in air or in a liquid, depending upon whether measurement was to be made of a solid–liquid–air contact angle or an interfacial contact angle. A cover, ground to fit, and having a very small hole in the center for the introduction of a

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(4) Friederich, *Fortschr. Chem. Physik physik. Chem.*, **18**, 5 (1926).

(5) Kuznetzov and Lavrentieva, *Z. Krist.*, **80**, 54 (1931).

(6) Reis and Zimmerman, *Z. physik. Chem.*, **102**, 298 (1922).

(7) Taylor, *Trans. Faraday Soc.*, **24**, 157 (1928).

(8) McBain, "The Sorption of Gases by Solids," George Routledge and Sons, Ltd., London, 1932, p. 295.

(9) Mack, *J. Phys. Chem.*, **40**, 159 (1936); Mack and Lee, *ibid.*, **40**, 169 (1936).

capillary pipet, was fitted over the top of the cell. The capillary pipet containing the liquid was next lowered by means of a ratchet and pinion device until it almost touched the surface of the solid. By applying air pressure at the top of the pipet, a drop of liquid was forced out on the solid, and was allowed to advance until it had a diameter of about 0.5 mm., when the pipet was removed by carefully raising it. A light source was placed behind the cell and the drop was observed with a microscope mounted in a horizontal position. The height and diameter of the drop were measured by means of a graduated ocular. On occasion, photographs were made of drops by means of a camera attached to the microscope.

Since individual drops show slight variations, a minimum of six individual determinations was made for each system investigated. If the angles of the individual drops varied by more than three or four degrees, eight or ten determinations were made.

Talc

The data obtained for talc are given in Table I. The data for contact angle in air, column 4, show that talc is neither strongly hydrophilic nor strongly organophilic since finite contact angles were measured on talc both with water and with a number of organic liquids. The data in column 6 show that talc must be considered to be organophilic in nature, however, since all the interfacial contact angles measured upon it (*i. e.*, measured through the water phase) were greater than 90°

TABLE I

CONTACT ANGLES IN AIR AND THE CALCULATED AND OBSERVED INTERFACIAL ANGLES OF A SERIES OF LIQUIDS ON TALC

$t = 25 \pm 1°$

	S_n (or S_3)	S_{n3}[a]	Θ_{1n} (or Θ_{13})	Θ_{1n3}, calcd.	Θ_{1n3},[a] obsd.
Water	72.1		86°		
Methylene iodide	50.2	48	53°	122°	121°
Alpha-bromonaphthalene	44.0	41.6	34°	139°	141°
Bromobenzene	35.9	39.6	12°	140°	142°
Acetylene tetrabromide	49.1	38.3	47°	138°	139°
Chlorobenzene	32.6	37.9	0°		140°
Toluene	28.1	36.1	0°		129°
Ethylene dibromide	38.1	36.0	26°	145°	145°
Benzene	28.2	34.6	0°		135°
Butyl acetate	24.1	13.2	0°		144°
Amyl alcohol	23.4	5.0	0°		100°
Benzyl alcohol	39.5	4.2[c]	32°	180°	122°
Water (satd. with benzyl alc.)	41.8[b]		42°		
Benzyl alcohol (satd. with water)	37.4[b]	4.2	32°	98°	122°

[a] Organic liquid "advancing." [b] Determined by the capillary rise method. All the other surface tension values given are from the literature. [c] The interfacial tension of benzyl alcohol against water was determined by means of the double cylinder method.[10] All the other interfacial tension values given are taken from the literature.

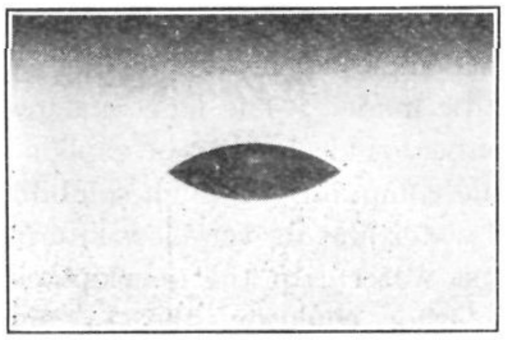

Fig. 1a.

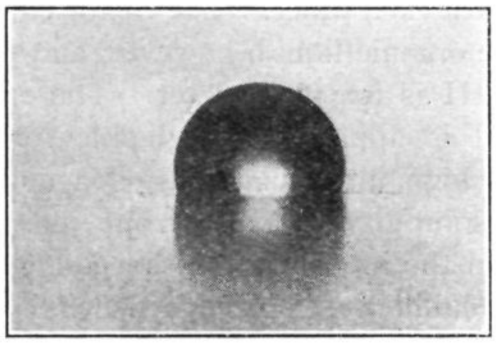

Fig. 1b.

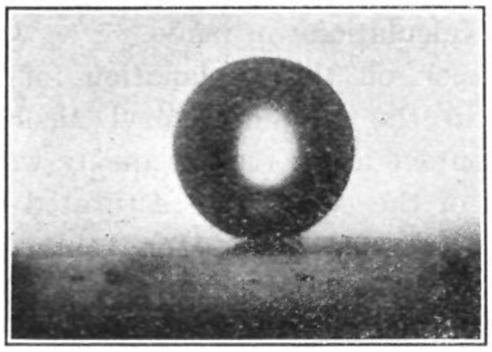

Fig. 1c.

The data in column 6 give the observed contact angles and the data in column 5 give the contact angles calculated from the Bartell–Osterhof equation (equation VIII). The observed interfacial angle values given in column 6 are all for organic liquid advancing angles. This does not mean that measurements were made on a dynamic advancing angle. The measurement was made on a static angle, but in each case the talc was first covered with water, the organic liquid was then introduced in the form of a drop which advanced over a surface previously wet by water. This method of procedure was considered best because

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(10) Bartell and Miller, THIS JOURNAL, **50**, 1961 (1928).

talc has a lower adhesion tension against water than against organic liquids, hence water will be more easily displaced from it by the organic liquid than will the organic liquid be displaced by water.

The agreement between the observed and calculated interfacial angles is remarkably close for all of the systems for which the calculation was possible with the single exception of the benzyl alcohol system. (Some of the organic liquids form zero contact angles with talc and the calculation could not be made.) The lack of agreement in the case of benzyl alcohol can be explained on the basis of the comparatively high solubility of the alcohol in water and its very low interfacial tension against water. In the development of the Bartell–Osterhof equation, the S_{1n} and S_{13} of equation VII are for organic liquid and water mutually saturated, for the two liquids are in contact with each other. The S_{1n} of equation II is for pure organic liquid, however, and the S_{12} of equation III is for pure water. The error thus introduced is apparently negligible for organic liquids of high interfacial tension against water and low solubility in water, but may become great when the interfacial tension is low and the mutual solubility appreciable. Benzyl alcohol has an interfacial tension value against water of only 4.2 dynes, as compared with values ranging from 34 to 48 dynes for the other five liquids for which the calculation was made.

As a check on this explanation for the discrepancy in the case of benzyl alcohol–water system, contact angle measurements were made with each of the two liquids saturated with the other. The data are included in Table I. It will be observed that the agreement between the observed and calculated interfacial angles is very much better than before, although not so close as was found for the other systems. Experimental error in the determination of any one of the four quantities, θ_{1n}, θ_{13}, S_n or S_3 introduces a large percentage error in the calculated θ_{1n3}, for the calculation involves the small difference between $S_3 \cos \theta_{13}$ and $S_n \cos \theta_{1n}$.

It seems justifiable to conclude that the Bartell–Osterhof equation is applicable to systems of insoluble solids when used in conjunction with liquids of low mutual solubility and high interfacial tension. It is probably applicable also to systems involving liquids of low interfacial tension, provided the mutual solubility effects of the liquids are taken into account.

As has been pointed out above, talc shows a marked difference in behavior from the harder solids previously examined in that it forms contact angles with water and with organic liquids of high surface tension. Talc also shows another marked difference from the harder solids previously examined. The data in column 6, Table I, show that the interfacial angles formed on talc by different organic liquids against water are different. The empirical equations of Bartell and Bartell[10] do not therefore apply to talc. Talc has been shown to be organophilic in nature, but its relative degree of organophilic nature cannot be measured on the convenient K_{n3} scale of Bartell and Bartell.[11]

Waxes and Resins

Many amorphous substances such as waxes and resins are soft and have low surface tension values. Their wetting characteristics would therefore be expected to be similar to those of the soft crystalline solid, talc.

A large number of substances, including paraffin, Japan wax, beeswax, spermaceti, a number of synthetic waxes including halogenated naphthalenes and biphenyls, and many natural and synthetic resins were investigated. Practically all of them were found to give large angles with water, and most of them gave fairly large angles with the organic liquids of high surface tension. Many of them were somewhat soluble in the organic liquids, however. Five substances in which the solubility effects were fairly low were chosen for detailed study, namely, Glyptal resin,[12] de Khotinsky cement (hard), carnauba wax, shellac and Opal wax 20.[13]

Fresh surfaces of these substances were obtained by melting them and allowing them to solidify on clean glass plates. The data obtained for contact angles in air and for interfacial contact angles are given in Table II. The solid–liquid–air angles are easily reproducible, since for any solid with a low surface tension value (*i. e.*, low free surface energy) there is very little tendency for the solid to be carried to a lower energy level by the adsorption of water vapor, atmospheric gases, etc. This fact is probably responsible for the good agreement found in the literature for the contact angle of water on paraffin as reported by different investigators. The interfacial angles were measured with organic liquid "advancing."

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[11] Bartell and Bartell, THIS JOURNAL, **56**, 2205 (1934).

[12] A commercial product known as Glyptal 1350.

[13] A commercial product.

TABLE II

CONTACT ANGLES IN AIR AND INTERFACIAL CONTACT ANGLES FORMED BY A SERIES OF LIQUIDS ON WAXES AND RESINS

	Glyptal resin		De Khotinsky cement		Carnauba wax		Shellac		Opal wax	
	θ_{1n}	θ_{n3}	θ_{1n}	θ_{n3}	θ_{1n}	θ_{n3}	θ_{1n}	θ_{n3}	θ_{1n}	θ_{n3}
Water	61°		106°		107°		107°		119°	
Methylene iodide	25°	90°	69°	122°	70°	128°	70°	133°	77°	123°
Acetylene tetrabromide	5°	133°	62°	130°	65°	140°	64°	128°	72°	136°
α-Bromonaphthalene	0°	88°	55°	123°	57°	146°	58°	126°	65°	149°
Benzyl alcohol	0°	160°	56°	137°	58°	142°	59°	132°	67°	134°
Ethylene dibromide	0°	90°	49°	137°	49°	145°	48°	146°	50°	151°
Bromobenzene	0°	96°	33°	138°	45°	148°	44°	135°	35°	156°
Chlorobenzene	0°	99°	29°	147°	35°	153°	35°	146°	27°	159°
Toluene	0°	87°	27°	148°	26°	154°	28°	145°	26°	161°
Butyl acetate	0°	130°	22°	143°	0–10°	166°	23°	156°	24°	153°
Amyl alcohol	0°	155°	19°	139°	0°	149°	20°	141°	25°	120°
Benzene		90°		136°		152°		144°		157°

The data obtained on waxes and resins cannot be considered as accurate data because of errors introduced by solubility effects. Measurements with the du Noüy Tensiometer showed that the surface tension of alpha-bromonaphthalene saturated with carnauba wax was practically the same as that of the pure liquid. The surface tension of water saturated with the wax was slightly lower than that of pure water, however, and the interfacial tension of alpha-bromonaphthalene against water was also lowered to some extent by the presence of carnauba wax.

Another factor to be considered is that the solids, being appreciably soluble in the organic liquids, are pitted when a drop of organic liquid is placed upon them. The surface under the drop is no longer plane. The measured angle is therefore not the true angle, for it is measured between the arc of the drop and the plane of the surface of the solid. Angles thus measured are reproducible and give an indication of the wetting properties of the solid, but they cannot be used for checking the Bartell–Osterhof equation. Since the interfacial angles measured on a given surface by water against different organic liquids were different, the indication is that the empirical equations of Bartell and Bartell[11] do not apply in these soft solids.

As has been pointed out, the behavior of soft solids can be explained on the basis of their low surface tension values. Waxes have very low surface tension values, the value for paraffin being given in the literature as 40 dynes. Measurements of the surface tension of molten waxes were made with the du Noüy Tensiometer. Temperature–surface tension curves were drawn and extrapolated to room temperature. They are shown in Fig. 2. The extrapolated values, which lie between 33 and 38 dynes (at 25°), should give a fairly accurate indication of the surface tension of the solid, for the curves are straight lines down to the point of solidification.

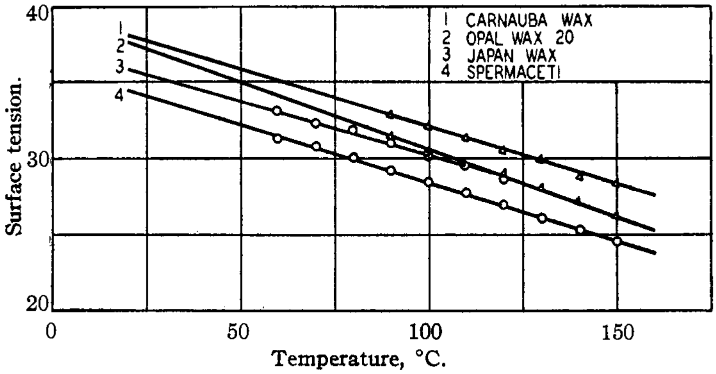

Fig. 2.

Since the waxes have surface tension values which are, presumably, lower than that of talc, they should give angles with liquids of fairly low surface tension which form zero angles on talc. This has been shown to be the case. Talc gave a small angle with bromobenzene (S_n = 35.9) and larger angles with liquids with higher surface tension values, but gave zero angles with liquids of lower surface tension. The waxes and resins gave measurable angles with butyl acetate (S_n = 24.1), and some of them gave measurable angles even with amyl alcohol (S_n = 23.4).

Summary and Conclusions

1. The wetting characteristics of talc and of a number of waxes and resins have been studied by measurements of the contact angles formed by small drops of liquid on these solids.

2. Both water and organic liquids (of high surface tension) form contact angles on these solids, thus indicating that the surface tension of these solids is low.
3. Soft solids of low surface tension are wetted less readily by liquids than are hard solids which possess a higher surface tension.
4. On talc, accurate measurements could be made of interfacial contact angles as well as of contact angles in air both with water and with organic liquids. This made possible the experimental testing of the Bartell–Osterhof equation relating adhesion tension and interfacial contact angles. This equation was found to hold.

ANN ARBOR, MICHIGAN

RECEIVED MAY 11, 1936

[CONTRIBUTION FROM THE METCALF CHEMICAL LABORATORY OF BROWN UNIVERSITY]

The Absorption Spectrum of Ethyl Methyl Ketone

BY A. B. F. DUNCAN, VICTOR R. ELLS AND W. ALBERT NOYES, JR.

The spectroscopy and photochemistry of acetone have been the subjects of numerous investigations. The spectrum consists of a broad absorption region extending from about 2200 to about 3200 Å. with a definite fine structure on the long wave end, a series of discrete bands extending from 1995 to about 1820 Å., and at shorter wave lengths other bands, some of which fitted a Rydberg formula predicting an ionization potential of 10.2 volts.[1] At still shorter wave lengths there is continuous absorption extending down to the limit of the observations made, about 800 Å. In the near ultraviolet fluorescence is observed, although attempts to find this phenomenon in the neighborhood of 1900 Å. failed.[2]

The next higher ketone is ethyl methyl ketone. The electronic structure of the carbonyl group must be very similar to that in acetone. However, the symmetry operations which may be performed on the two molecules differ considerably. If the methyl group forming part of the ethyl group is considered to execute a perfectly symmetrical rotation around the adjacent carbon–carbon bond, there will be only one symmetry operation aside from the identity, namely, reflection in the plane containing the carbonyl group and the two adjacent carbon atoms. However, due to various types of interaction between the different parts of the molecule, this particular rotation might not be expected to be completely symmetrical so that ethyl methyl ketone must be considered to possess a very low order of symmetry.

Experimental Procedure and Discussion of Results

The methyl ethyl ketone used in these experiments was prepared by the acetoacetic ester synthesis, using acetoacetic ethyl ester and methyl iodide. It was purified by formation of the sodium bisulfite compound, dried with potassium carbonate and fractionally distilled.[3]

For investigation of the near ultraviolet absorption a Hilger E_3 spectrograph was used together with Eastman III-O and 33 plates.

The absorption spectrum of the liquid in this region has been investigated, but that of the vapor has not been reported. Two absorbing columns of 1 and 10 meters with pressures of 3 to 86 mm. (the vapor pressure at 25°) were used. At the highest pressure the absorption extended from approximately 3200 to 2400 Å. No trace of vibrational fine structure was observed under any conditions.

Ethyl methyl ketone shows strong fluorescence when illuminated with approximately monochromatic 3130 Å. radiation. The fluorescence viewed with a hand spectrograph appeared to consist of a continuous band in the green. We were unable to obtain photographs of the fluorescence with the E_3 spectrograph, but the matter is being pursued further.

In view of this fluorescence, particular care was used in making the absorption measurements to vary the pressures over a wide range, and at each

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(1) (a) Damon and Daniels, THIS JOURNAL, **55**, 2363 (1933); (b) Scheibe, Povenz and Linstrom, *Z. physik. Chem.*, **B20**, 297 (1933); (c) Crone and Norrish, *Nature*, **132**, 241 (1933); (d) Norrish, Crone and Saltmarsh, *J. Chem. Soc.*, **1934**, 1456; (e) Noyes, Duncan and Manning, *J. Chem. Phys.*, **2**, 717 (1934); (f) Duncan, *ibid.*, **3**, 131 (1935).

(2) Howe and Noyes, THIS JOURNAL, **58**, 1404 (1936).

(3) The authors wish to express their appreciation to Professor C. B. Wooster for suggesting the method of synthesis and supervising its execution.