trum of phthalamic acid in deuterium oxide exhibited bands at 1694 and 1625 cm.$^{-1}$, corresponding to carboxylic acid and amide groups. The carboxylic acid band remained constant with time but the amide band was slowly replaced by a new carboxylate band at 1560 cm.$^{-1}$.[6]

The kinetics of the hydrolysis of phthalamic acid in water are shown in Table I.

TABLE I

THE KINETICS OF HYDROLYSIS OF PHTHALAMIC ACID[a,b]

| $p$H | $k_{\text{obs}} \times 10^4$ (sec.$^{-1}$) | | | |
|---|---|---|---|---|
| | 47.3° | 35.0° | 24.8° | 24.8°[d] |
| 1.3 | 2.35 | | | |
| 1.8 | 2.37[c] | 0.66 | 0.21 | 0.31 |
| 2.6 | 2.32 | | | |
| 3.4 | 1.70 | | | |
| 4.2 | 0.58 | | | |
| 5.0 | 0.11 | | | |

[a] Measurements made at 292 mμ with a Beckman DU spectrophotometer. [b] $\Delta H^{\ddagger}$ 20.7 kcal./mole; $\Delta S^{\ddagger}$ $-12.4$ e.u. For benzamide, $\Delta H^{\ddagger}$ 22.8 kcal./mole; $\Delta S^{\ddagger}$ $-13.9$ e.u. Apparently a more positive entropy is not the sole cause of the increased rate of intramolecular catalysis. [c] Variation in the ionic strength from 0.016 to 0.12 $M$ produced no change in the rate constant. [d] Deuterium oxide solution.

The variation in rate with $p$H indicates kinetic dependence on the undissociated phthalamic acid and independence of external hydrogen ion. The hydrolysis of phthalamic acid is about $10^5$ faster than the hydrolysis of benzamide with a comparable concentration of hydrogen ion.[7] This large rate enhancement suggests that the *ortho*-carboxylic acid group does not exert a substituent effect but rather catalyzes the amide hydrolysis by a direct intramolecular process.

A similar internal mechanism occurring in the hydrolysis of glycyl-L-asparagine and L-leucyl-L-asparagine was suggested to proceed through an internal proton transfer.[8] However, the relatively high basicity of amides precludes this as the full explanation.[9] It is suggested that this intramolecular process is a general acid–general base catalyzed reaction, and that the carboxylic acid performs a dual role, similar to a bifunctional catalyst,[10] attacking the carbonyl carbon atom of the amide, and simultaneously donating a proton to the departing ammonia molecule, with the formation of phthalic anhydride. An alternative mechanism which must be considered is a preequilibrium involving the transfer of the proton to the amide nitrogen, followed by reaction of the zwitterion to form the anhydride. These mechanisms differ in the relative position of the proton and the distribution of charge in the transition state. The effect of $D_2O$ on the rate favors the latter path. The lack of dependence of the rate on the ionic strength of the medium suggests that the distribution of charge in the transition state is similar to that in the reactant. An anhydride intermediate is postulated to form in other general basic catalyses,[3] including some intramolecular catalyses,[11] and is known to be rapidly hydrolyzed by water.[12]

The hydrolysis of an amide, which is specific hydronium and hydroxide ion-catalyzed in intermolecular catalysis,[13] appears to be subject to general acid-base catalysis in this intramolecular process.[14]

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[6] G. Ehrlich, THIS JOURNAL, **76**, 5263 (1954); G. Ehrlich and G. B. B. M. Sutherland, *ibid.*, **76**, 5268 (1954).

[7] B. S. Rabinovitch and C. A. Winkler, *Can. J. Research*, **20B**, 73 (1942).

[8] S. J. Leach and H. Lindley, *Trans. Faraday Soc.*, **49**, 921 (1953). These examples do not show as pronounced rate enhancements or as favorable stereochemistry as the present case.

[9] A. R. Goldfarb, A. Mele and N. Gutstein, THIS JOURNAL, **77**, 6194 (1955).

[10] C. G. Swain and J. F. Brown, Jr., *ibid.*, **74**, 2538 (1952).

[11] H. Morawetz and P. E. Zimmering, *J. Phys. Chem.*, **58**, 753 (1954); J. D. Chanley, E. M. Gindler and H. Sobotka, THIS JOURNAL, **74**, 4347 (1952), and references cited therein. Only the carboxylate ion participates in these reactions.

[12] A. C. D. Rivett and N. V. Sidgwick, *J. Chem. Soc.*, **97**, 1683 (1910).

[13] M. L. Bender, unpublished results.

[14] The author acknowledges valuable discussions with Drs. E. M. Kosower, G. J. Buist and R. W. Taft, Jr.

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## FORMATION OF CYCLOPROPANE FROM METHYLENE AND ETHYLENE

*Sir:*

Recently a suggestion was made[1] that cyclopropane is the immediate product of reaction between methylene and ethylene, even though propylene is the identified product, the explanation being that cyclopropane so formed has a very short lifetime because of large energy content and therefore isomerizes into propylene.

The only experimentally proven formation of the cyclopropane ring in the gas phase by the reaction of methylene with an olefin is that of *cis*-1,2-dimethylcyclopropane.[2] In the liquid phase other olefins have been shown to form three-membered rings when reacting with methylene.[2,3,4] In all these cases methylene has been shown also to attack the carbon–hydrogen bond.

Ketene was used as the source for photochemically produced methylene. A low pressure mercury arc and a Pyrex reaction vessel insured that the 3130 Å. lines of the mercury spectrum were mainly responsible for the reaction.[5] Ketene–ethylene mixtures in the ratio 1:7.5 were photolysed at room temperature at a series of initial pressures. About 25% of ketene was decomposed in each run. Since methylene reacts faster with ethylene than with ketene under the experimental conditions chosen,[6,7] there should be very little complication due to the latter reaction.[6,7,8] The reaction products condensable in liquid nitrogen were separated by means of vapor chromatography and the three-carbon fraction was then analyzed mass spectrometrically.

Cyclopropane was found, the relative yield increasing with pressure as shown in Fig. 1. The solid line drawn is consistent with the mechanism:

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[1] G. B. Kistiakowsky and Kenneth Sauer, THIS JOURNAL, **78**, 5699 (1956).

[2] P. S. Skell and R. C. Woodworth, *ibid.*, **78**, 4496 (1956).

[3] W. von E. Doering, R. G. Buttery, R. G. Laughlin and N. Chaudhuri, *ibid.*, **78**, 3224 (1956).

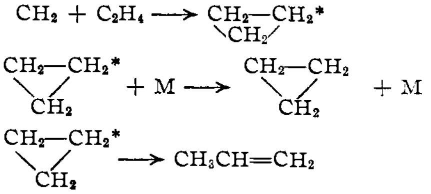
[4] W. von E. Doering and P. LaFlamme, *ibid.*, **78**, 5447 (1956).

[5] A. N. Strachan and W. A. Noyes, Jr., *ibid.*, **76**, 3258 (1954).

[6] G. B. Kistiakowsky and N. W. Rosenberg, *ibid.*, **72**, 321 (1950).

[7] G. B. Kistiakowsky and W. L. Marshall, *ibid.*, **74**, 88 (1952).

[8] R. A. Holroyd and W. A. Noyes, Jr., *ibid.*, **78**, 4831 (1956).



which, aside from the activation step, is identical with that of the thermal isomerization of cyclopropane. The lifetime of the "hot" cyclopropane molecules formed in these experiments is found to be *ca.* one-eightieth of that of those formed thermally. The greater reactivity of these energy rich cyclopropane molecules as compared with the thermally "hot" molecules is to be expected from the theories of both Kassel[9] and Slater.[10]

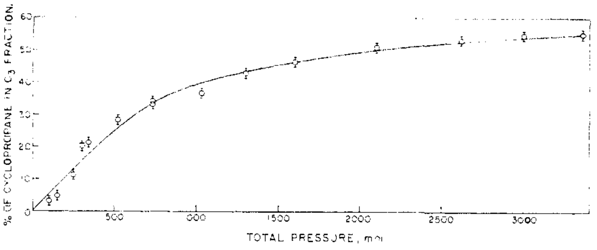


Fig. 1.

The yield of cyclopropane at high pressures tends asymptotically to a value close to 0.6. This suggests that, as in other cases investigated,[2,3,4] two competing reactions are taking place: the attack on the double bond with formation of cyclopropane in one elementary act, and the attack of the carbon–hydrogen bond. The latter leads directly to the formation of propylene.

Further experiments on the formation of three-membered rings in the gas phase and on the effects of inert gases are in progress.

It is a pleasure to thank Professor G. B. Kistiakowsky for suggesting these experiments and for many helpful discussions.

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(9) L. S. Kassel, "The Kinetics of Homogeneous Gas Reactions," (The Chemical Catalog Company) Reinhold Publ. Corp., New York, N. Y., 1932.

(10) N. B. Slater, *Proc. Roy. Soc.* (*London*), **194A**, 112 (1948).

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## INFLUENCE OF DISSOLVED AIR ON OPTICAL DENSITY MEASUREMENTS OF WATER SOLUTIONS

*Sir:*

In the course of studies employing measurements of optical densities, *D*, of water solutions, we have found significant variations in *D* in the region of 2000 Å. which are due to light being absorbed by variable amounts of atmospheric oxygen dissolved in the solutions. This effect is large enough to be important in the calculation of the absorbances of the other components of the solutions, but it is entirely separate from spectral changes which may occur as the result of oxidation of solute species by atmospheric oxygen. We trust that this means of reporting the effect will serve to bring it most quickly to the attention of others engaged in work of this kind.

The optical density of a 10-cm. depth of conductivity water which has been saturated with air is higher than that of the same water through which helium, nitrogen, or carbon dioxide has been bubbled by 0.09 in *D* at 2000 Å., 0.03 at 2100 Å., 0.01 at 2200 Å. and by less at longer wave lengths of ultraviolet and visible light up to at least 8000 Å. The very small oxygen content of the commercial gases employed was found to increase in the order we have cited them, but was low enough in all cases to give the same final values of *D* for the solution.

Saturation of conductivity water at 25° with oxygen at 1 atm. was found to increase *D* above the value for air saturated water by 0.47 in *D* at 2000 Å. for 10 cm. light paths, and by lesser amounts at longer wave lengths; at 2500 Å. the increase amounts to about 0.01. The effects are reversible. Typical results are presented in Fig. 1.

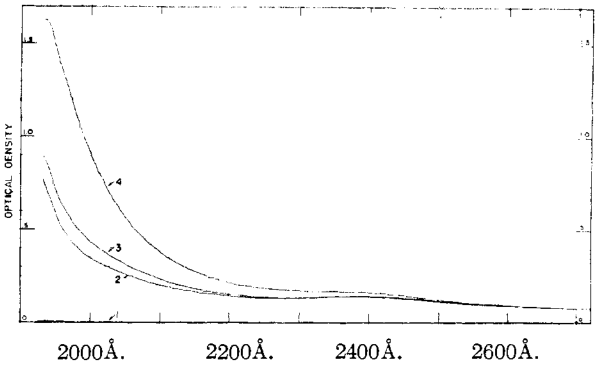

Fig. 1.—Optical densities at 25° referred to air: (1) of air and (2), (3), and (4) of a fused quartz absorption cell of 10 cm. between windows which has been filled with conductivity water freed from air and oxygen, saturated with air at 1 atm., and saturated with oxygen at 1 atm., respectively.

Similar effects have been reported for solutions of oxygen in organic solvents[1,2] such as hexane.

The absorption of light by an equivalent amount of oxygen gas at 2000 Å. and longer wave lengths is presumably negligible.[3]

The extent of the effect of dissolved oxygen on *D* depends upon the following variables: wave length of the light, composition and temperature of the solution, and the partial pressure of the oxygen gas over the solution.

In the case of alkaline solutions, the values of *D* are also affected up to even longer wave lengths by the carbon dioxide in the air, but the effect of the carbon dioxide is not reversible because of the formation of significant amounts of carbonate and bicarbonate as long as the solution remains alkaline.

We have found that objectionable gases such as oxygen may be removed from liquids most effectively with commercial helium, but the commercial grade of prepurified nitrogen is also satisfactory in many cases.

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(1) D. F. Evans (a) *J. Chem. Soc.*, 343 (1953); (b) *J. Chem. Phys.*, **23**, 1424 (1955).

(2) A. U. Munck and J. F. Scott, *Nature*, **177**, 587 (1956).

(3) G. Herzberg, *Can. J. Phys.*, **30**, 185 (1952).