suming that this is the true freezing point and that the Δt/mole per cent. impurity is 0.20° as given in reference 1, the purity of their sample is estimated to be 74% and ours is 99.5 mole per cent.

The infrared spectrum of the sample of isopropylcyclopropane used to determine the physical constants gave the absorption maxima in Table II.

TABLE II

λ, microns	3.40	4.92	5.26	6.77	6.96	7.21
Transmission, %	5	72	74	6	19	11
λ, microns	7.30	7.45	7.58	7.74	8.21	8.57
Transmission, %	11	58	39	14	33	18
λ, microns	8.84	9.05	9.56	9.78	9.94	10.46
Transmission, %	40	45	15	10	17	14
λ, microns		10.82	11.01	11.39	12.18	13.48
Transmission, %		35	22	12	13	46

NATIONAL ADVISORY COMMITTEE FOR
AERONAUTICS V. A. SLABEY
LEWIS FLIGHT PROPULSION LABORATORY P. H. WISE
CLEVELAND, OHIO L. C. GIBBONS

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POLAROGRAPHIC DETERMINATION OF THE MOLECULAR WEIGHT OF SERUM ALBUMIN BY ITS EFFECT ON THE DIFFUSION CURRENT OF METHYL ORANGE

Sir:

The purpose of this note is to describe the great difference in the effect of gelatin and serum albumin on the diffusion current of 10^{-4} M methyl orange in a 0.01 N phosphate buffer of pH of 7.2, or in very dilute potassium chloride solutions and to show that the complex formation between serum albumin and methyl orange can be studied quantitatively by the polarographic method.

The polarographic behavior of methyl orange in water in the presence of various supporting electrolytes without proteins shows several complicated features which are the subject of further work. Under the conditions described below in the presence of proteins these complications were eliminated.

A small amount of gelatin (0.01%) reduces i_d by 10%, but larger amounts (up to 1%) exert hardly any further effect. The addition of serum albumin causes a continuous reduction of i_d until the protein concentration is about 0.5%. These observations can be interpreted in agreement with the results of Klotz,[1] *et al.*, who found that serum albumin combines, but that gelatin does not combine with methyl orange. Polarographically we found that at a concentration of about 0.5% serum albumin practically all the methyl orange (10^{-4} M) has combined with the protein. Application of the Ilkovič equation gave a value of the diffusion coefficient of the complex of 9.05×10^{-7} cm.^{2} sec.$^{-1}$ at 25°. Using this value in the Stokes–Einstein equation yields a value of 66,000 for the molecular weight, which is in good agreement with reported values of molecular weight (68,000 to 70,000) of serum albumin. The decrease of i_d of methyl orange by serum albumin at various concentrations can be made use of in the calculation of the binding constant.

The effect of serum albumin on the diffusion current of 10^{-4} M methyl orange in 0.01 to 0.05 N potassium hydroxide solutions is negligibly small. This again is in agreement with the results of Klotz,[1] who found that serum albumin does not combine with the dye at these high pH values.

More extensive polarographic studies on the effect of proteins in the native and denatured state on various dyes and other compounds are planned.

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SCHOOL OF CHEMISTRY OF THE W. STRICKS
UNIVERSITY OF MINNESOTA I. M. KOLTHOFF
MINNEAPOLIS, MINN.

RECEIVED MARCH 7, 1949

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[1] I. M. Klotz, F. M. Walker and R. B. Pivan, THIS JOURNAL, **68**, 1486 (1946); Klotz, *ibid.*, **68**, 2299 (1946); Klotz, Triwush and Walker, *ibid.*, **70**, 2935 (1948); Klotz and Urquhart, *J. Phys. Coll. Chem.*, **53**, 100 (1949).

INHIBITING EFFECT OF NITRIC OXIDE ON THE THERMAL DECOMPOSITION OF DIETHYL KETONE

Sir:

Previous studies on the thermal decomposition of acetone[1] and methyl ethyl ketone[2] established the fact that the rates are uninhibited by the addition of nitric oxide. Instead, small amounts of nitric oxide, probably due to its reaction with the ketene intermediate, cause marked catalysis and this effect increases with the amount of inhibitor added. Propylene, on the other hand, reduces the rates of both reactions to a limiting value, indicating that free radicals are indeed present.

In our present investigations we find that small amounts of nitric oxide reduce the rate of decomposition of diethyl ketone to a definite, limiting value which is readily reproducible. The figure, where ρ is the rate with a given amount of inhibitor, ρ_0, that with none, and ρ_∞, the limiting rate, shows that the amount of inhibition is essentially independent of ketone pressure, indicating that the radical producing reaction must be of the first order. No catalytic effect was observed up to 20 mm. partial pressure of nitric oxide. The mean chain length is 2.0, the same value as determined for the thermal decomposition of methyl ethyl ketone with propylene. Preliminary experiments reveal that the decomposition of methyl propyl and methyl isopropyl ketones are uninhibited by nitric oxide.

The inhibiting effect of nitric oxide on diethyl ketone is in striking contrast to its effect on other ketones investigated so far. One would logically expect the primary decomposition reactions to be basically similar, and certainly methyl ethyl and diethyl ketones should initially produce the same kind of chain propagating radicals. This surpris-

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[1] Smith and Hinshelwood, *Proc. Roy. Soc.* (*London*), **A183**, 33 (1944).

[2] Waring and Mutter, THIS JOURNAL, **70**, 4073 (1948).

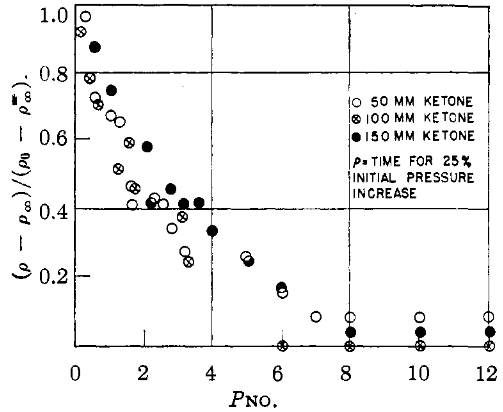

Fig. 1.

ing effect of nitric oxide on diethyl ketone may be explained by postulating that (1) the decomposition of diethyl ketone initially produces a free radical different from that of other ketones; or, (2) the mechanism of this decomposition is radically different from that of the other ketones, perhaps no ketene intermediate being formed. While both possibilities are feasible, the former appears more likely, since a comparison of the inhibiting effects of nitric oxide and propylene on ketone decompositions strongly suggests that the efficiency of these inhibitors is dependent upon the type of free radical present.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CONNECTICUT
STORRS, CONNECTICUT
CHAS. E. WARING
CLEMENT S. BARLOW

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