NOTES

The Production of Radicals by the Illumination of Diacetyl with λ 4358 Å.

By H. W. Anderson and G. K. Rollefson

In a recent paper[1] we remarked that we had obtained some evidence that photo-activated diacetyl molecules might react with nitric oxide. This statement was based on the observation that when diacetyl is illuminated at room temperature with light of wave length 4358 Å. of such intensity that the rate of decomposition is negligible, a much more rapid reaction occurs when nitric oxide is present. It seemed desirable to undertake further experiments to ascertain whether this effect was actually due to a reaction of activated molecules or whether the molecules were actually dissociated by this light but the net decomposition was kept low by a high efficiency of recombination of the radicals formed. One experiment of this kind is to illuminate mixtures of diacetyl and acetaldehyde with this radiation, to which acetaldehyde is transparent, at temperatures such that free radicals will initiate decomposition chains in the acetaldehyde. In this communication we wish to report the results of experiments of this kind and discuss their significance.

The apparatus and analytical techniques have been described previously. The diacetyl was a commercial product, the acetaldehyde an especially pure sample prepared by Dr. W. L. Roth. The light source was a quartz capillary arc,[2] from which the light of wave length 4358 Å. was isolated by means of the Zeiss Filter C, and the 4047 Å. radiation by the filters CG 579 and CG 306.

Diacetyl–acetaldehyde mixtures are thermally stable at temperatures as high as 155°, although the presence of small amounts of air will cause an oxidation to occur. When an approximately equimolal mixture of the two substances is illuminated by the 4358 Å. line, an easily measured reaction occurs even at a temperature as low as 100°. The reaction results in the disappearance of acetaldehyde and a small amount of diacetyl with the formation of carbon monoxide and methane in nearly equivalent amounts, together with a small amount of hydrogen. The rate of the reaction increases several-fold when the temperature is increased from 100 to 150°. The wave lengths 4358 and 4047 Å. were found to be equally effective at equal light absorption.

In a typical experiment at 150°, a mixture of 11.06×10^{-5} mole of acetaldehyde and 9.70×10^{-5} mole of diacetyl in a cylindrical 120-cc. vessel was illuminated with the 4358 line for fifteen minutes. The analyses showed that 0.99×10^{-5} mole of acetaldehyde and not more than 0.10×10^{-5} mole of diacetyl disappeared, 1.00×10^{-5} mole of carbon monoxide, 0.80×10^{-5} mole of methane and 0.14×10^{-5} mole of hydrogen were formed. (Because the diacetyl and acetaldehyde were separated by distillation at $-78°$ only an upper limit can be given for the amount of diacetyl decomposed.)

The combination of the evidence presented here and the results previously obtained at room temperature with nitric oxide in the system leads to the conclusion that diacetyl can be dissociated by the addition of the small energy supplied by the quantum of wave length 4358 Å. (64 kcal.). It is possible that the dissociation is induced by the added gas, nitric oxide or acetaldehyde, or that some of the energy necessary for the dissociation is supplied by the internal energy in the molecule before photoactivation but the fact still remains that an appreciable number of radicals are formed by the addition of this low energy. The properties of the radicals are in accord with those previously given for acetyl except that to account for the low efficiency of this wave length in decomposing pure diacetyl, it must be assumed that the energy possessed by the radicals immediately after formation is not sufficient to bring about their spontaneous dissociation.

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Magnetic Susceptibilities of cis and trans Decalin

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Through the courtesy of Professor W. F. Seyer, of the University of British Columbia, the authors obtained samples of pure cis and trans decalin

(1) Anderson and Rollefson, This Journal, 63, 816 (1941).
(2) Atwood and Rollefson, J. Chem. Phys., 9, 506 (1941).

(decahydronaphthalene).[1] Magnetic measurements on these substances were made by methods previously described.[2] The following data were obtained at 35°.

	Density, d^{35}_4	Susceptibility, $\chi \cdot 10^6$
cis decalin	0.8867	−0.774
trans decalin	.8607	−0.779

It is not surprising that the susceptibilities are almost exactly equal. The small difference is, however, believed to be significant. According to Van Vleck[3] the susceptibility per gram mole of a polyatomic molecule without resultant spin is given by

$$\chi_{mol} = -\frac{Le^2}{6mc^2}\sum \bar{r^2} + \frac{2}{3}L\sum_{n'\neq n}\frac{|m^0(n';n)|^2}{h\nu(n';n)}$$

where the symbols have their usual significance.

This expression consists of the familiar diamagnetic part and of a temperature-independent paramagnetic part. The latter term is generally believed to be negligible in most molecules. The present results suggest that the term may be detectable when, as in the case of *cis* and *trans* decalin, the only difference is one of symmetry. As anticipated, the paramagnetic term is larger for the *cis* form in which atomic orbits are probably slightly more distorted than in the *trans* form.

(1) Seyer and Walker, THIS JOURNAL, **60**, 2125 (1938).

(2) Selwood, *ibid.*, **61**, 3168 (1939); Preckel and Selwood, *ibid.*, **62**, 2765 (1940).

(3) Van Vleck, "The Theory of Electric and Magnetic Susceptibilities," Oxford University Press, New York, N. Y., 1932, p. 275.

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Preparation and Properties of Dimethylphosphine

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In the course of an investigation on the polymerization of some derivatives of trimethylaluminum,[1] a pure sample of dimethylphosphine was required. According to Hofmann,[2] pure dimethylphosphine can be obtained by (1) heating phosphonium iodide, methyl iodide and zinc oxide in a sealed tube in the molar ratio $2PH_4I:2MeI:1ZnO$, (2) treating the product with water whereby phosphine and monomethylphosphine are evolved, and (3) liberating the dimethylphosphine by addition of an alkali. We have found that the product thus obtained is contaminated with trimethylphosphine, which can be separated from the di-

(1) Davidson and Brown, THIS JOURNAL, **64**, 316 (1942).

(2) Hofmann, *Ber.*, **4**, 605 (1871).

methylphosphine by fractionation *in vacuo*. Hofmann's procedure for the preparation and isolation of dimethylphosphine is considerably simplified by the use of modern high vacuum techniques.

Nine grams of methyl iodide, 10.3 g. of phosphonium iodide and 2.6 g. zinc oxide were heated for eight hours at 100° in a bomb tube. The tube was opened, connected to a vacuum line, and water added to drive off the phosphine and monomethylphosphine. The addition of gaseous ammonia (in excess) to the residue liberated a mixture of dimethylphosphine and trimethylphosphine. This mixture was subjected to fractional distillation in a simple, partial reflux column (wire-spiral type) with the still head at −95 to −100° ("pumped down" carbon dioxide–ether) and the still pot at −80°. Under these conditions[3] the distillate could be bled off as a vapor directly into the vacuum apparatus, in the absence of an inert atmosphere or a mercury bubbler. From 90 cc.[4] of the mixture there was isolated 71 cc. of pure dimethylphosphine. The last fractions were shown to consist chiefly of trimethylphosphine by vapor tension measurements ($p = 14$ mm. at −46°).[5]

The purity of the sample of dimethylphosphine was established by several observations. Its molecular weight was 62.3 (a 25.5-cc. sample weighed 70.5 mg.) as compared with the calculated value of 62.0; it was tensimetrically homogeneous ($p = 30$ mm. at −47°); and the observed value of the vapor pressure with 99% of the total sample in the vapor phase agreed very well with that calculated from values obtained at lower temperatures. A series of vapor tension measurements from −47.0 to 15.0° were made; the data fit the equation, $\log p = -(1370/T) + 7.539$, as shown in the following table.

VAPOR TENSIONS OF DIMETHYLPHOSPHINE

Temp., °C.	−47.0	−41.9	−30.9	−21.2	0	15.0
p in mm., obsd.	30	40.5	75	127	338	595
p in mm., calcd.	30	41	76	127	336	598

From these data, the boiling point is calculated to be 21.1°;[6] ΔH (vap.), 6.27 kcal.; and Trouton's constant, 21.2.

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(3) The vapor tension of the dimethylphosphine is of the order of 2–3 mm. at −80° and several tenths of a mm. at −95 to −100°.

(4) Measured as a gas at standard conditions.

(5) Rosenbaum and Sandberg, THIS JOURNAL, **62**, 1622 (1940).

(6) Hofmann reports 25°. His value for the boiling point of trimethylphosphine is also high (see reference 5).