

## NOTES

**The Production of Radicals by the Illumination of Diacetyl with  $\lambda$  4358 Å.**

BY H. W. ANDERSON AND G. K. ROLLEFSON

In a recent paper<sup>1</sup> 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,<sup>2</sup> 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 equimolar 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  $11.06 \times 10^{-5}$  mole of acetaldehyde and  $9.70 \times 10^{-5}$  mole of diacetyl in a cylindrical 120-cc. vessel was illuminated with the 4358 line for fifteen minutes. The analyses showed that  $0.99 \times 10^{-5}$  mole of acetaldehyde and not more than  $0.10 \times 10^{-5}$  mole of diacetyl disappeared,  $1.00 \times 10^{-5}$  mole of carbon monoxide,  $0.80 \times 10^{-5}$  mole of methane and  $0.14 \times 10^{-5}$  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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RECEIVED OCTOBER 8, 1941

**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).