

fyng corresponding states behavior. If we accept that the Kihara core model gives an adequate representation of the molecular interactions of the heavy rare gases, as a growing body of evidence now indicates, then the results of this paper indicate that the assump-

tion of the additivity of the potential seems to be valid for thermodynamic calculations of the fluid phase within the range so far studied.

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Photoenolization of Biacetyl

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Irradiation of biacetyl either in hexane or in aqueous solution below 3100 Å (to give the second excited singlet state) gives a product which is probably an enol. Biacetyl in a *cis* form could give an enol which would be stabilized by internal hydrogen bonding. The quantum yield of enol formation is about 0.12. In the vapor phase a similar product is formed. At 4358 Å, enol formation at room temperature either in solution or in the vapor state is essentially zero but is appreciable at 100°. The compound tentatively identified as the enol inhibits both the phosphorescence and the decomposition upon exposure to wavelengths which give the first excited singlet state. Since oxygen does not quench the fluorescence of biacetyl but quenches both the phosphorescence and the formation of the enol, it is suggested that the enol arises from the triplet state of biacetyl. If the triplet state is a precursor for enol formation, the data suggest that an activation energy is necessary and hence that high vibrational levels of the triplet state are involved.

Introduction

The photochemistry of biacetyl has received much attention both in the vapor phase and in solution.^{2a} The results of Porter^{2b} and those of Bäckström and Sandros^{2c} indicate that all initially formed singlet molecules at 4358 Å which do not either dissociate or fluoresce cross over to the triplet state. Presently known processes do not account for all of the triplet-state molecules.

Fluorescence from biacetyl when excited to the first singlet state either in the liquid or in the gas phase is very small, with a quantum yield of about 0.0025.³ Thus, crossover to the triplet state at 4358 Å occurs with a yield greater than 0.99. Phosphorescence from the triplet state has a yield of about 0.15. Decomposition at this wavelength is negligible at room tem-

perature, although there is some dissociation which results from interaction between two excited molecules.⁴ The dissociation yield increases rapidly with increase in temperature.

Some unidentified product from biacetyl at 4358 Å

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(2) (a) W. A. Noyes, Jr., G. B. Porter, and J. E. Jolley, *Chem. Rev.*, **56**, 49 (1956); (b) G. B. Porter, *J. Chem. Phys.*, **32**, 1587 (1960); (c) H. J. L. Bäckström and K. Sandros, *Acta Chem. Scand.*, **14**, 48 (1960).

(3) G. M. Almy and P. R. Gillette, *J. Chem. Phys.*, **11**, 188 (1943). The fluorescent yield in dilute solution may be as high as 0.01. F. Wilkinson and J. T. Dubois, *ibid.*, **39**, 377 (1963).

(4) W. A. Noyes, Jr., W. A. Mulac, and M. S. Matheson, *ibid.*, **36**, 880 (1962); G. F. Sheats and W. A. Noyes, Jr., *J. Am. Chem. Soc.*, **77**, 4532 (1955).

0.391

0.0087

0.0062

0.0004

0.0025

0.0019

0.0042

-0.0015

0.350

0.0186

0.0211

0.0234

0.0258

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0.0340

0.0376

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B. Brown and
J. Chem. Phys.,

, 413 (1964);
7, 897 (1964).