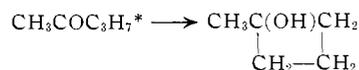
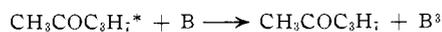


process I. In addition, it was noted that the related process⁴



is also quenched by biacetyl. The emission measurements which were carried out in our laboratory indicate that, as noted by Michael and Noyes, a strong phosphorescence emission appears when biacetyl is added to 2-pentanone. However, the fluorescence emission from 2-pentanone, which has a maximum between 4100 and 4300 Å. (as measured on a Hilger F/4) and which is unaffected by the addition of oxygen up to 490 mm. does not vary by more than 2%. This conclusion is based on the observation that the light emitted by various 2-pentanone-biacetyl mixtures (total pressure of 30 mm.) containing 1 mm. of oxygen is identical with that emitted by pure 2-pentanone. Thus, one is forced to conclude that only triplet excited biacetyl is formed in the energy transfer process in the photolysis of 2-pentanone at 3130 Å., and that consequently process I occurs *via* a triplet excited state.



In a similar way, by measuring the emission of acetone-biacetyl, 2-butanone-biacetyl, and 3-methyl-2-butanone-biacetyl mixtures, both in the presence and in the absence of oxygen, we concluded that, as already noted for acetone,⁵ only the ketone molecule excited to the triplet state transfers its energy to biacetyl. The relative efficiency of the energy transfer, which is apparently strongly dependent on the dissociative lifetime of the excited ketone molecule, was found to vary according to the sequence: acetone > 2-butanone > 2-pentanone > 3-methyl-2-butanone.

Additional data, which will be reported in the near future, also indicate that because of the efficient vibrational deactivation of the excited state at higher densities, the photoelimination from 2-pentanone and 2-hexanone, as well as the formation of the cyclic alcohols, can be quenched by biacetyl more readily in the liquid phase than in the gas phase. The quenching efficiency in the liquid phase is independent of wave length from

(4) P. Ausloos and R. E. Rebert, *J. Am. Chem. Soc.*, **83**, 4897 (1961).

(5) J. Heicklen and W. A. Noyes, Jr., *ibid.*, **81**, 3858 (1959).

2537 to 3130 Å. but is strongly dependent on the temperature which determines the dissociative lifetime of the excited ketone molecule.

It may be noted that, in the study of Borkowski and Ausloos,⁶ as in the case of the ketones, the fluorescence emitted by *n*-butyraldehyde is not quenched by the addition of biacetyl, clearly showing that a triplet state is involved. The latter conclusion is corroborated even more conclusively by a recent study⁷ on the photolysis of acetone-aldehyde mixtures in which it is shown that at 3130 Å. the emission from the triplet state of acetone is quenched by *n*-butyraldehyde and that there is a corresponding photosensitization of the elimination of ethylene from *n*-butyraldehyde. It should be pointed out that from the results concerning the benzophenone-sensitized decomposition of the aldehydes recently reported,² no firm conclusions can be drawn unless quantum yields are determined. Chain reactions involving the abstraction of the hydrogen from the acyl group of the aldehyde, which should be intensity dependent, may lead to an apparent low olefin yield.

In the case of the benzophenone-ketone mixtures referred to by Borrell, it has not been established that energy transfer from benzophenone to the ketone occurs. Actually, energy transfer to the ketone may be endothermic⁸ with the resulting effect that photoreduction of the benzophenone may become of importance.

It is clear that a generalization such as the one made recently² is not warranted. As noted before,⁶ it is quite possible that, although at 3130 and 3340 Å. photoelimination of olefins can occur from a triplet state, at wave lengths shorter than the ones used in the investigations reported here, the same process may conceivably occur from a singlet excited state as well. Also, the probability that at any given wave length the same process will occur from either a triplet or a singlet state may depend on the structure of the compound under consideration.

(6) R. P. Borkowski and P. Ausloos, *ibid.*, **84**, 4044 (1962).

(7) R. E. Rebert and P. Ausloos, *ibid.*, in press.

(8) G. S. Hammond, N. J. Turro, and P. A. Leermakers, *J. Phys. Chem.*, **66**, 1144 (1962).

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BOOK REVIEWS

Fast Reactions in Solution. By E. F. CALDIN. John Wiley and Sons, Inc., 605 Third Ave., New York 16, N. Y. 1964. 306 pp. 14 × 22 cm. Price, \$7.50.

This book contains a much needed and very interesting compendium of the various methods that have been used to study reactions from a range of seconds to microseconds. It also includes, as well, a chapter on the "general topics" which is interesting and useful although not closely related to the instrumental theme of the book. The book is replete with examples of the application of rapid reaction techniques to various chemical and biochemical reactions. It is well filled with references from which the reader may draw to obtain a more penetrating evaluation.

If one is to find a fault, it would be mostly in the depth of discussion of particular methods, but, of course, not much depth can be expected of a 300-page compendium which attempts to cover all methods. Nevertheless, a few examples are useful. The mixing chamber illustrated on page 31 is excellent for the rather low flow velocities for which it was designed, but fails seriously when cavitation of the flow stream must be considered. The fact that cavitation provides a limit to the time range of flow apparatuses, should have been discussed.

Another omission is in the biological applications of the flash methods; while strongly influenced by the excellent flash photolysis studies of Gibson, the author seems to have omitted only a description of the flash work of H. T. Witt, and flash studies of visual pigments merit only a small paragraph.

Throughout the book, one feels a lack of emphasis on problems arising from the scarcity of biochemicals, and often methods are cited for their rapidity and with little regard as to whether or not biochemicals are available in sufficient amounts. But the book is well worth having for the researcher and the student, and surely meets the author's plan "that the reader will be able to form an impression of the possibilities, limitations and achievements of each technique." The book will be useful to many, and one hopes that it will inspire some to take up the fascinating field of rapid reactions.

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Noble Gases and Their Compounds. By G. J. MOODY and J. D. R. THOMAS, Welsh College of Advanced Technology, Cardiff. The Macmillan Co., 60 Fifth Ave., New York 11, N. Y. 1964. 62 pp. + vii. 13.5 × 20.5 cm. Price, \$2.00.

After a ten-page introduction including historical background and factual data about the noble gases, pages 11 through 52 discuss the recent developments in noble gas chemistry. More than half of the 134 references end with (1962) or (1963).

The authors' stated purpose of bringing together into a convenient volume information from many different journals has certainly been accomplished. The book can easily be read in one evening and gives a quick survey of the early part of the recent interesting developments in a field of chemistry quite nonexistent before 1962. The writing was too early to include much on the now extensive aqueous chemistry of xenon, and theoretical discussions of binding have been largely ignored.

The careful reader will be bothered by numerous mistakes such as crediting a theoretical chemist with a warning about the hazards of XeO₃ in a publication dated earlier than the actual discovery (by someone else) of XeO₃, quoting a m.p. of 100° when the quoted authors said "was observed not to melt up to 100°," etc.

More serious than these mistakes and typographical errors is the lack of critical evaluations and even of careful reading of the papers referred to. As an example of this lack, on page 19 there are quoted values of 10 and of 15.3 kcal./mole for the enthalpy of sublimation of XeF₄ as if they were equally reliable. In fact, the former was just a guess made for the purpose of a rough calculation, and the latter was a measured value.

Many of the references quoted were preliminary announcements published quickly as notes because of the great interest in the new field. A number of these notes include mistakes that were later corrected in "Noble Gas Compounds," University of Chicago Press, a report of a conference held in April, 1963. Although the present authors include this book among their references, they evidently did not have time to read it. If they had, they could have corrected a number of these errors in the literature instead of serving to perpetuate them.

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Inorganic Ultramicroanalysis. By I. P. ALIMARIN and M. N. PETRIKOVA, U.S.S.R. Academy of Sciences. The Macmillan Co., 60 Fifth Ave., New York 11, N. Y. 1964. xv + 151 pp. 14.5 × 22.5 cm. Price, \$6.00.

According to the authors, this small book represents an attempt to present a systematic summary of the techniques of ultramicroanalysis, which they define as the analysis of masses of 10⁻⁸–10⁻¹² g., using volumes of 10⁻³ to 10⁻⁶ ml. Soviet work in the field—particularly that of the authors—is strongly represented, of course.

About two-thirds of the book is devoted to methods of qualitative analysis. The manipulative techniques described are essentially those developed by Benedetti-Pichler many years ago. The tests suggested for the qualitative detection of various elements use conventional reagents: thiocyanate for iron, cobaltinitrate for potassium, chloride for silver, and so on.

Some minor alterations of the nonsulfide scheme of qualitative microanalysis published some 10 years ago by C. L. Wilson and his colleagues are suggested.

The chapter dealing with methods of separation is more interesting. Electrolytic separations using either platinum or mercury cathodes are described in some detail, and directions are given for electrolyzing vanadium-copper-iron and vanadium-chromium solutions, with subsequent detection of the separated elements at levels of 10 to 100 nanograms (millimicrograms).

A miniature ion-exchange column is referred to. A photograph of the column and fraction collector is shown, but details of column dimensions and flow rates are not given (many other techniques mentioned in the book are described with similar vagueness).

The section on quantitative analysis covers both gravimetric and volumetric methods. Ultramicrobalances and methods for their calibration are treated briefly in what amounts essentially to a summary of published American experience in the field.

However, in volumetric ultramicroanalysis—especially in the employment of potentiometric and amperometric methods—there is evidence of very good work, and some elegant techniques are described. Supporting data are presented in the form of titration curves.

In addition to a not-unreasonable number of typographical errors, the book contains other errors which indicate either carelessness or a lack of understanding of the material treated.

Thus in discussing the theoretical limits of application of ultramicroanalysis, the authors use as a sole criterion statistical adherence to the laws of chemical equilibrium. Hence 10⁶ molecules are sufficient for a quantitative analysis accurate to 0.1% ($\sqrt{10^6}/10^6 = 0.1\%$). Little thought is required to discover the general inapplicability of this criterion.

On page 3, equation 3 is incorrectly stated to represent the fractional change in vapor pressure of a liquid as a function of the curvature of its surface. The authors have confused differences in pressure with differences in vapor pressure.

On page 97, the cantilever ultramicrobalance ("fishpole balance") is erroneously called a torsion balance, and a drawing of a cantilever balance (Figure 35) is mislabeled accordingly. (Perhaps the reviewer is unduly perturbed by this error, since the drawing is reproduced without credit from one of his papers.)

On the same page, the quantity *J* appearing in equation 13 is defined as the moment of inertia of the fiber, whereas actually it is the moment of inertia of its cross section about the line of intersection of the neutral plane with the cross section.

The general impression created is that the work done by the authors in volumetric ultramicroanalysis is quite good, but that in attempting their more general survey of the field of ultramicroanalysis, they have been hasty and uncritical.

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The Chemistry of Imperfect Crystals. By F. A. KROGER, Philips' Research Laboratories, Eindhoven, The Netherlands. John Wiley and Sons, Inc., 605 Third Ave., New York 16, N. Y. 1964. 1039 pp. + xiv. 6.5 × 9 cm. Price, \$33.00.

Traditionally, chemistry has dealt more with reactions between atoms and molecules in gaseous or liquid media than in solids. Although chemists as long ago as 1914 were aware that non-stoichiometric solids (Bethollides) existed, it was not until attempts to explain their electrical properties were made that the great importance of crystal imperfections (impurities and lattice defects) became evident. Gudden and Pohl (1920–1930) were among the first to recognize this. However, it was Schottky and Wagner who showed how statistical thermodynamics and the law of mass action could be usefully applied to reactions in crystals involving vacancies and electrons, as well as atomic species.

Parallel to this development of the chemistry of crystal imperfections, there has been a corresponding, and even greater, in terms of numbers of publications, development of the physics of crystal imperfections beginning with A. H. Wilson's energy band model in 1931. The gap between the chemistry and physics of crystal imperfections has steadily closed with time, and today the common meeting ground is the microscopic attack on the nature of the imperfections themselves as disclosed chiefly by optical and electron spin resonance investigations backed up by crystal field theory.

Kroger's book, as the title states, is concerned primarily with the chemistry of imperfections. In this pursuit, it is by far the most comprehensive and complete work of its kind published to