

Fig. 1.—Electron spin resonance spectra of butyryl (upper) and isobutyryl (lower) anion radicals.

e.s.r. signals of the isobutyryl radical in Fig. 2 (lower) were produced in an isobutyroin solution containing 0.01 *M* benzophenone, exposed to 3660 Å., the $n \rightarrow \pi^*$ band of benzophenone. Note that Fig. 1 (lower) and Fig. 2 (lower) were obtained with the same spectrometer settings of microwave power and amplification, and that Fig. 2 shows even C^{13} lines of the radical. Clearly, there is an order of magnitude increase in the radical concentration in the sensitized run. Comparison of the upper and lower curves of Fig. 2 shows that the benzophenone ketyl anion radical $(C_6H_5)_2C=\dot{O}$ is also present in the sensitized experiment. The spectrum of the ketyl radical (Fig. 2, upper) was observed in an alcohol-water solution of 0.01 *M* benzophenone and 0.5 *M* NaOH exposed to 3660-Å. light. This radical has been previously observed.⁸

Two tentative mechanisms may be suggested for the photosensitized results:

(1) Triplet-triplet energy transfer from the excited benzophenone to the isobutyroin anion, followed by the enolization and oxidation of the latter. A singlet-singlet transfer can be ruled out, since the singlet state of the former ($26,000 \text{ cm.}^{-1}$)⁹ is lower than that of the latter (centered at $34,500 \text{ cm.}^{-1}$). The position of the triplet of isobutyroin is unknown but may be assumed to be close to that of acetone, *i.e.*, approximately $24,500 \text{ cm.}^{-1}$.¹⁰ Hence, energy transfer from the benzophenone triplet ($24,250 \text{ cm.}^{-1}$)⁹ is conceivable. In the framework of this mechanism, the formation of the ketyl radical would be an independent process, just as it is in the solution devoid of acyloin.

(2) The effective transfer of an electron from the acyloin anion to the excited, electrophilic benzophenone molecule (probably triplet), resulting in the reduction of the latter and the oxidation of the former without an enolization step. This over-all reaction could proceed either through an actual electron transfer, yielding

(8) P. B. Ayscough and R. Wilson, *J. Chem. Soc.*, 5412 (1963). The excitation energy is not specified in this work.

(9) V. L. Ermolaev, *Soviet Phys.-Usp.* (Engl. Transl.), **6**, 333 (1963).

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

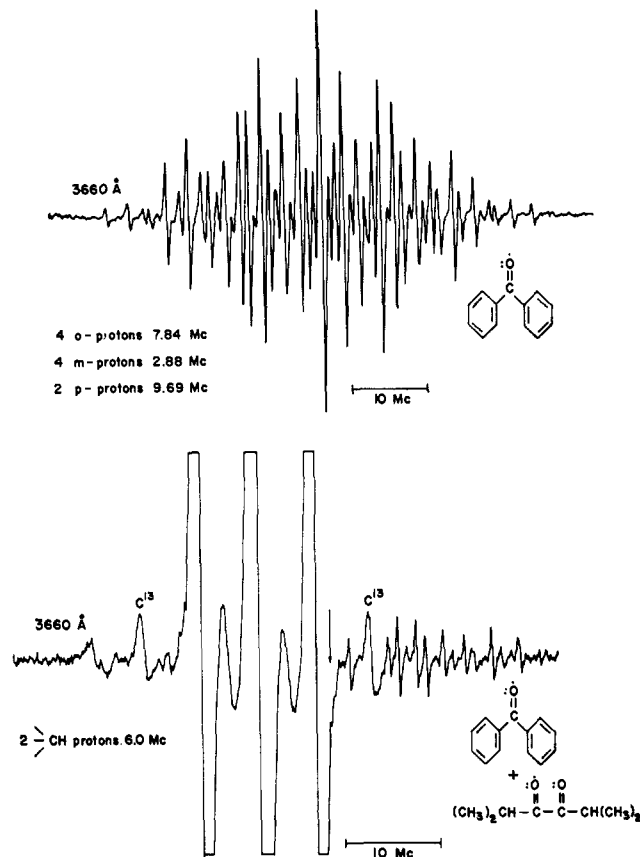


Fig. 2.—Electron spin resonance spectra of the benzophenone ketyl (upper and lower) and isobutyryl anion (lower) radicals; arrow indicates position of center line of the ketyl radical.

directly $(C_6H_5)_2C=O$, $R-C(=O)-R$, and water, or *via* a hydrogen-atom transfer.¹¹ In the latter case, $(C_6H_5)_2\dot{C}-OH$ and the isobutyryl radical would form first, and the former would then give $(C_6H_5)_2C=\dot{O}$ and H_2O in basic solution.

Further work on these phenomena, including the use of other sensitizers, is now in progress.

(11) J. N. Pitts, R. L. Letsinger, R. P. Taylor, J. M. Patterson, G. Recktenwald, and R. B. Martin, *J. Am. Chem. Soc.*, **81**, 1068 (1959); W. M. Moore, G. S. Hammond, and R. P. Foss, *ibid.*, **83**, 2789 (1961).

(12) In some former publications, C. Heller was used.

SCIENTIFIC LABORATORY
FORD MOTOR COMPANY
DEARBORN, MICHIGAN

HANAN C. HELLER¹²

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Structure in the Ionization Efficiency Curves of Ar_2^+ by Pulsed Mass Spectrometry

Sir:

Previous observations of the ionization efficiency curves of Ar_2^+ ¹⁻⁸ (using continuous ion repulsion)

- (1) J. A. Hornbeck and J. P. Molnar, *Phys. Rev.*, **84**, 621 (1951).
- (2) J. S. Dahler, J. L. Franklin, M. S. B. Munson, and F. H. Field, *J. Chem. Phys.*, **36**, 3332 (1962).
- (3) W. Kaul, U. Lauterbach, and R. Fuchs, *Naturwiss.*, **47**, 353 (1960).
- (4) W. Kaul and R. Fuchs, *Z. Naturforsch.*, **15a**, 326 (1960).
- (5) W. Kaul and R. Taubert, *ibid.*, **17a**, 88 (1962).
- (6) F. H. Field, H. N. Head, and J. L. Franklin, *J. Am. Chem. Soc.*, **84**, 1118 (1962).
- (7) M. S. B. Munson, J. L. Franklin, and F. H. Field, *J. Chem. Phys.*, **37**, 1790 (1962).
- (8) M. S. B. Munson, J. L. Franklin, and F. H. Field, *J. Phys. Chem.*, **67**, 1542 (1963).

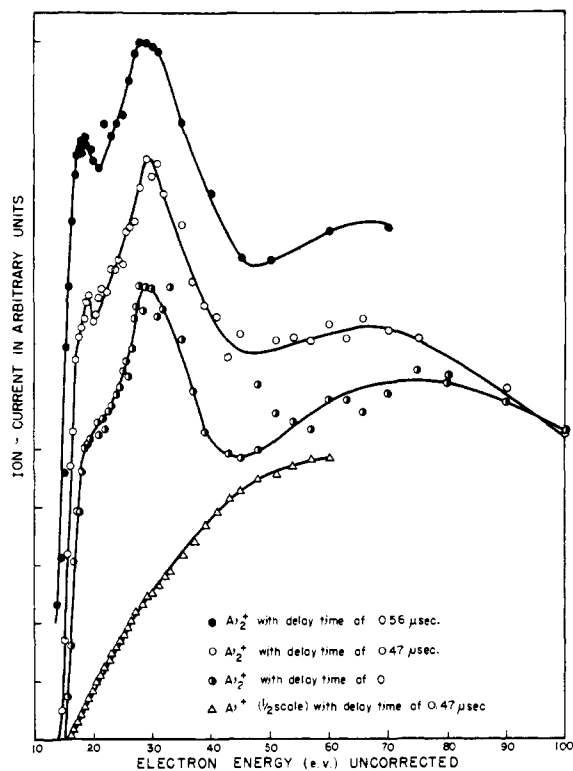


Fig. 1.—Ionization efficiency curves in argon as a function of delay time.

have not revealed the structure to be expected in view of Kaul's⁹ finding that three excited states of argon, having lifetimes of 5.4×10^{-7} , 2.0×10^{-6} , and 1.9×10^{-5} sec., are involved; rather only one sharp peak at 18 e.v., characteristic of a single excitation function for a forbidden transition, has been reported. Comes¹⁰ has reported, however, a second peak at about 30 e.v. which contributes increasingly to Ar_2^+ as the pressure is raised. In view of the conditions used,¹⁰ it is difficult to understand the previous failures¹⁻⁸ to observe this peak.

We wish to report here confirmatory evidence of Kaul's⁹ and Comes'¹⁰ conclusions which we have obtained by pulsed mass spectrometry, a technique first used to measure thermal rate constants of ion molecule reactions.¹¹ In our experiments, using a Bendix 14-101 time-of-flight mass spectrometer, a short electron beam pulse is followed after a variable time delay by a large ion-extraction pulse. Ionization efficiency curves of Ar_2^+ were obtained for several delay times at source pressures of 5-8 μ . As shown previously,¹² zero time delay corresponds to about 0.1 μ sec. of reaction time. Ar_2^+ formation can occur during draw-out, but such ions will show up only as a tailing on the long-time side of the $m/e = 80$ peak. The longest delay time used is less, by a factor of at least three, than the primary ion transit time to a wall.

The results are shown in Fig. 1 and 2 in which the Ar_2^+ and Ar^+ ion currents are plotted to different scales, and in which the Ar_2^+ ordinates have been shifted vertically to avoid overlapping of the curves. The normal ionization efficiency curves for Ar^+ demon-

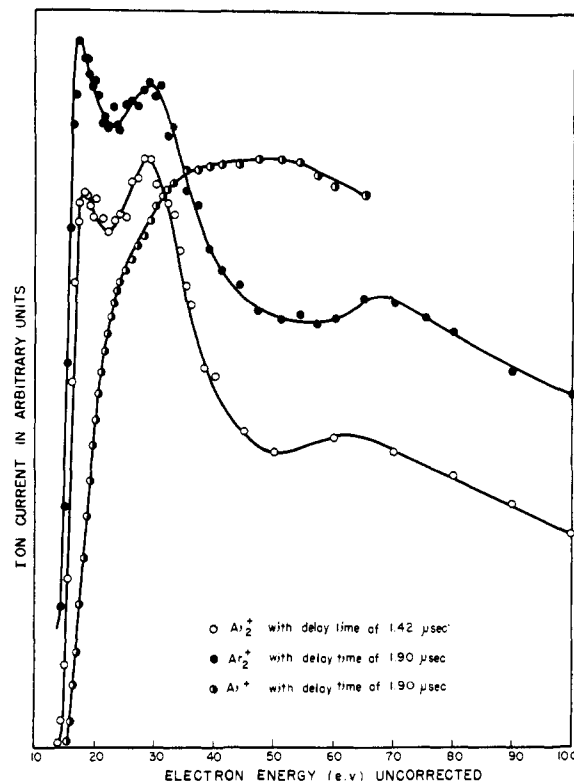
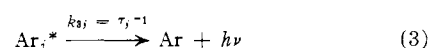
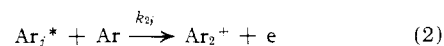
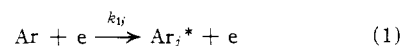


Fig. 2.—Ionization efficiency curves in argon as a function of delay time.

strate that the structures in the Ar_2^+ curves are not due to instrumental conditions in the source. The two maxima at about 18 and 28 e.v. (which are in agreement with Comes' observations¹¹) are characteristic of excitation functions for optically forbidden transitions, while the broad maximum in the region of 60-70 e.v. is characteristic of the excitation function for optically allowed transitions.¹³

The effect of delay time on the shape of the ionization efficiency curves can be understood in terms of the lifetimes measured by Kaul³ and the kinetic aspects of Ar_2^+ formation. Consider the reaction scheme²



where $j = 1, 2$, and 3 , and τ_j is the radiative lifetime of the j th state. Assuming that at $t = 0$, $[\text{Ar}_2^+] = 0$, it is easily shown that

$$[\text{Ar}_2^+] = [\text{Ar}] \sum_{j=1}^3 \frac{k_{1j}k_{2j}[\text{Ar}_j^*]_0}{1\tau_j^{-1} + k_{2j}[\text{Ar}]} [1 - e^{-(\tau_j^{-1} + k_{2j}[\text{Ar}])t}] \quad (4)$$

where the k 's are the specific reaction rates, and $[\text{Ar}_j^*]_0$ is the concentration of the j th excited state at zero reaction time. In the steady state of continuous ion repulsion, $t = \infty$.

Consideration of Kaul's measured lifetimes⁹ and the mean values reported for k_{2j} ^{9,12} indicates that at source pressures up to 10 μ , τ_j^{-1} either dominates or is comparable to $k_{2j}[\text{Ar}]$ for all j . According to eq. 4, the relative contributions of states with small τ to

(9) W. Kaul, "VIII International Conference on Ionization Phenomena in Gases, Paris, 1963," p. 169.

(10) F. J. Comes, ref. 9, p. 159.

(11) V. L. Tal'roze and E. L. Frankevich, *Zh. Fiz. Khim.*, **34**, 2709 (1960).

(12) F. W. Lampe and G. G. Hess, *J. Am. Chem. Soc.*, **86**, 2952 (1964).

(13) H. S. W. Massey and E. H. S. Burhop, "Electronic and Ionic Impact Phenomena," Oxford University Press, New York, N. Y., 1952, p. 147 ff.

Ar_2^+ production will be more important at short reaction times (short delay times) because of the exponential term. As reaction time (or delay time) is increased, however, eq. 4 indicates that the relative contributions of states with larger τ will increase. In other words, the excited states with large τ , having not yet radiated, will make more collisions in the longer time available for reaction. This is, in fact, observed in Fig. 1 and 2 in the growth of the peak at 18 e.v. with respect to that at 28 e.v., and the growth of both of these with respect to the broad peak at 60–70 e.v. In fact, the ratio of the 18-e.v. peak to the 65-e.v. peak increases approximately linearly with delay time. This would be expected from (4) if the peak at 18 e.v. is due to a state long-lived with respect to delay time, while the 65-e.v. peak is due to a state short-lived with respect to delay time. We, therefore, assign the peaks at 18, 28, and 60–70 e.v. to the excitation functions for those states observed by Kaul³ to have lifetimes of 1.9×10^{-5} , 2.0×10^{-6} , and 5.4×10^{-7} sec., respectively. We suggest that the first two peaks represent excitation to optically forbidden states and the latter to an optically allowed state with the observed ionization efficiency curve being a superposition of the three excitation functions. As Kaul³ has pointed out, a specific assignment of these states to known argon terms is not now possible.

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DEPARTMENT OF CHEMISTRY
THE PENNSYLVANIA STATE UNIVERSITY
UNIVERSITY PARK, PENNSYLVANIA

PHILIP M. BECKER
F. W. LAMPE

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Pentachlorocyclopentadienyl Cation, a Ground-State Triplet

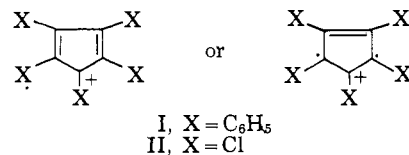
Sir:

In cyclic conjugated systems with $4n$ π -electrons and C_3 or greater symmetry, it is predicted that the ground state may be a triplet (*i.e.*, have two unpaired electrons). As has been reported elsewhere,¹ pentaphenylcyclopentadienyl cation (I), a symmetrical derivative of the 4 π -electron cyclopentadienyl cation, has a low-lying ($E_a = +550$ cal./mole) triplet state, although its ground state is a singlet.² It seems likely that the singlet is favored in I because the large π -system decreases electron correlation and the complex structure allows easy distortion of symmetry. Such factors are found to an even greater extent in heptaphenylcycloheptatrienyl anion, in which a low-lying triplet state was not detected.³ Accordingly, the possibility remains that in simpler derivatives of 4 π -electron systems the ground state will be a triplet. We wish to report that pentachlorocyclopentadienyl cation (II) is apparently such a case.

(1) R. Breslow, H. W. Chang, and W. A. Yager, *J. Am. Chem. Soc.*, **85**, 2033 (1963).

(2) Bulk susceptibility measurements indicate <10% triplet at 4°K. and <6% at 213°K.

(3) R. Breslow and H. W. Chang, *J. Am. Chem. Soc.*, **84**, 1484 (1962), and subsequent e.s.r. studies.



Mixing hexachlorocyclopentadiene and SbF_5 (10 moles excess) at room temperature produced a dark green viscous oil which, when quickly transferred to a sample tube and cooled to 77°K., exhibited an electron spin resonance spectrum typical of a triplet species (Fig. 1), along with evidence of an ordinary radical at $g = 2$. The signal for a $\Delta m = 2$ transition at 1362

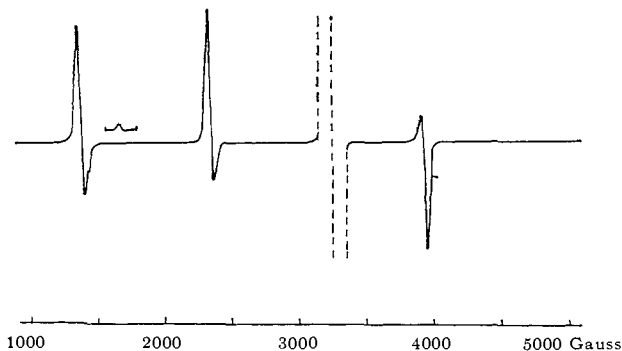


Fig. 1.—E.s.r. spectrum of C_5Cl_5^+ . This spectrum shows all the reproducible features of several runs; the very weak z -lines are shown at the fields at which they appear with much greater amplification.

gauss, xy -component $\Delta m = 1$ satellites at 2340 and 3944 gauss, and very weak z -component $\Delta m = 1$ satellites at 1675 and 4865 gauss, indicates that a triplet is present with $D = 0.1495$ cm^{-1} and $E < 0.002$ cm^{-1} .⁴ Similar values were obtained at 4°K.⁵ There the $\Delta m = 2$ and xy lines were observed at the low microwave power levels needed to minimize saturation. The value of D , which measures the interaction of the two unpaired electrons, is as expected larger than the 0.1050 cm^{-1} for I, but smaller than values for carbenes⁶ or nitrenes⁷ in which the two electrons are largely localized on the same atom (*e.g.*, cyclopentadienylidene,^{6b} $D = 0.4089$ cm^{-1}). The zero value of E indicates that the triplet is isotropic in the xy molecular plane; this is expected for a species with pentagonal symmetry, and was also observed for I, but nonzero values of E are easily detected for triplets^{6,7} which lack such symmetry. The vanishing of E at 4°K. as well indicates that the symmetry is inherent in the triplet and not due to rotation in the xy -plane. Thus the triplet species being observed here must almost certainly be II.⁸

When the SbF_5 solution is quenched in methanol, the major products (total 92%) are four dimeric perchlorocyclopentenones⁹ (analysis, infrared, ultraviolet)

(4) Cf. E. Wasserman, L. C. Snyder, and W. A. Yager, *J. Chem. Phys.*, **41**, 1763 (1964).

(5) We would like to thank Mr. W. A. Yager and Mr. R. M. R. Cramer for their aid in the liquid helium measurements.

(6) (a) A. M. Trozzolo, R. W. Murray, and E. Wasserman, *J. Am. Chem. Soc.*, **84**, 4990 (1962); (b) E. Wasserman, L. Barash, A. M. Trozzolo, R. W. Murray, and W. A. Yager, *ibid.*, **86**, 2304 (1964).

(7) E. Wasserman, G. Smolinsky, and W. A. Yager, *ibid.*, **86**, 3166, (1964); **84**, 3213 (1962).

(8) The possibility that it is instead a cyclopentadienyl cation with some or all of the chlorines replaced by fluorines is excluded by the observation that no fluorine is present in any of the products from methanol quenching.

(9) The structures of these compounds will be discussed in the full publication.