is governed by a single parameter X, which gives the ratio of the mean angular momentum in centrifugal motion of the complex to that in rotation of the reactant and product molecules. The data correspond to $X \sim 2$, a value consistent with the model.[11] The peak $\hat{f}$ of $P(f)$ is also related to the centrifugal energy of the complex; the model predicts $\hat{f} \simeq (\mu/\mu')^{3/2}(E/E_{tot})$, where μ and μ' are the reduced masses of the reactants and products, $E = 3.0$ kcal/mol, the most probable collision energy, and $E_{tot} \simeq 13$ kcal/mol, the total available energy (mean reactant energy plus reaction exoergicity). For $f > \hat{f}$, the model predicts $P(f) \simeq (1 - f)^n$, the classical vibration–rotation energy level density evaluated at the transition state. The exponent $n = 2$, $^3/_2$, or 1, for a "tight" linear, a strongly nonlinear, or a "loose" transition state, respectively.[9,10] The data agree closely with the predicted peak $\hat{f} \simeq 0.05$ and with $n = 2$.

According to the RRKM lifetime formula, the complex should not persist for as long as one rotation unless it were stable by roughly 20 kcal/mol or more. The obvious choice is the known, stable Br_2O molecule.[12] This has a symmetric, strongly bent equilibrium geometry and according to Walsh's molecular orbital correlation diagrams[13] (and analogy to H_2O, etc.) should have a singlet ground state. Since the reactants approach on a triplet surface, such a complex would require a triplet → singlet transition, although the products can depart on either a singlet or triplet surface. The large reaction yield seems more compatible with a triplet than a singlet complex. Also, orbital correlations predict that insertion of the O atom into the Br_2 bond will be inhibited by a large energy barrier, as in the reactions of hydrogen or halogen atoms with halogen molecules.[8]

An unsymmetric O–Br–Br structure for the complex appears likely. This is consistent with the "electronegativity ordering rule," derived from the Walsh scheme and supported by much empirical evidence,[8] which predicts that the preferred geometry of an XYZ complex has the least electronegative atom in the middle. The analogous O–Cl–Cl molecule has been found in a matrix isolation study[14] and the isoelectronic ion $(F–Cl–Cl)^+$ is also known,[15] but the bond angle, spin state, and stability of these species are not known. An O–Br–Br complex, even if considerably nonlinear, might well have a triplet ground state. In constructing his diagrams, Walsh emphasized that the orbital he denoted by $\bar{a}'$-$3\bar{\sigma}$ might cross the $\bar{a}''$-$3\bar{\pi}$ and $\bar{a}'$-$3\bar{\pi}$ orbitals and lie below them at large bond angles.[16] If so, a triplet ground state is predicted for linear O–X–X, and in a better approximation this might remain the ground state over a substantial range of bond angles.[17]

The O + ICl and O + IBr reactions offer evidence for the unsymmetric complex. If not precluded by geometry, a statistical complex would strongly favor formation of ClO or BrO, which are exoergic by ~13 kcal/mol, rather than IO, which is almost thermoneutral. However, the electronegativity rule predicts an O–I–X complex. We find the ICl and IBr reactions give IO with a very large yield but no detectable ClO or BrO.

The O + I_2 and O + Cl_2 reactions have also been studied (not yet with velocity analysis) and again the reactive scattering is consistent with a persistent complex.[18] For O + Cl_2 we find an activation energy of ~3 kcal/mol, in accord with a flow tube experiment.[19] The O + F_2 reaction (not yet studied) would be expected to prefer the symmetric OF_2 geometry rather than O–F–F, since O is less electronegative than F. Thus it seems likely to require a fairly large activation energy.[20]

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(11) See discussion in ref 1–3 and Figure 11 of ref 3.

(12) C. Campbell, J. P. M. Jones, and J. J. Turner, *Chem. Commun.*, 888 (1968).

(13) A. D. Walsh, *J. Chem. Soc.*, 2266 (1953).

(14) M. M. Rochkind and G. C. Pimentel, *J. Chem. Phys.*, **46**, 4481 (1967).

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(16) We thank D. A. Dixon (Harvard University) for discussions and a CNDO-UHF calculation for triplet linear O–Cl–Cl which finds the $3\bar{\sigma}$ orbital energy is indeed about 24 kcal/mol below the $3\bar{\pi}$ orbital.

(17) L. C. Allen in "Sigma Molecular Orbital Theory," O. Sinanoglu and K. B. Wiberg, Ed., Yale University Press, New Haven, Conn., 1970, p 227.

(18) R. Grice has independently studied O + I_2, private communication, Cambridge University, England.

(19) M. A. A. Clyne and J. A. Coxon, *Trans. Faraday Soc.*, **62**, 2175 (1966).

(20) In a flow tube study O + F_2 gave no detectable reaction under conditions where O + Br_2 gave a very large yield. See M. Kaufman and C. E. Kolb, *Chem. Instrum.*, **3**, 175 (1971).

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Benzyne[1]

Sir:

In view of the intense chemical interest in benzyne,[2] it is surprising that physical studies of this intriguing molecule have been limited to observation of the ultraviolet absorption spectrum and mass spectrometric measurements.[3,4]

The limiting factor in physical studies has been the preparation of benzyne under conditions suitable for observation. We wish to describe the preparation of benzyne under conditions conducive to general spectroscopic observation.

Irradiation of phthaloyl peroxide (**1**) matrix isolated in argon at 8°K gives carbon dioxide, benzpropiolactone (**2**), and a ketoketene (**3**) (Scheme I).[5] Prolonged irradiation produces benzyne (**4**) and carbon dioxide. The identity of the product is established by an independent synthesis (infrared comparison) and chemical trapping.

Irradiation of neat benzocyclobutenedione (**5**) at 77°K[6] gives the dimers reported by Staab and Ipaktschi.[7] Decarbonylation of **5** is observed on irradiation in ethanol at room temperature[8] and matrix isolated in

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(1) Photochemical Transformations. LII.

(2) R. W. Hoffmann, "Dehydrobenzene and Cycloalkynes," Academic Press, New York, N. Y., 1967, and references cited therein.

(3) R. S. Berry, G. N. Spokes, and M. Stiles, *J. Amer. Chem. Soc.*, **84**, 3570 (1962); **82**, 5240 (1960).

(4) R. S. Berry, J. Clardy, and M. E. Schafer, *ibid.*, **86**, 2738 (1964); M. E. Schafer and R. S. Berry, *ibid.*, **87**, 4497 (1965).

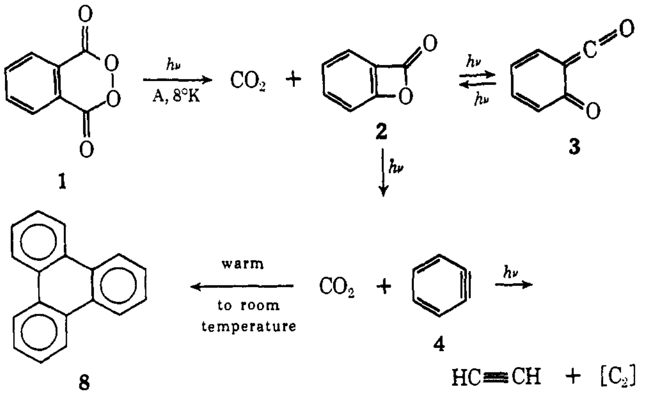
(5) O. L. Chapman, C. L. McIntosh, J. Pacansky, G. V. Calder, and G. Orr, *ibid.*, **95**, 4061 (1973).

(6) O. L. Chapman and C. L. McIntosh, *Chem. Commun.*, 1162 (1971).

(7) H. A. Staab and J. Ipaktschi, *Chem. Ber.*, **101**, 1457 (1966); *Tetrahedron Lett.*, 583 (1966).

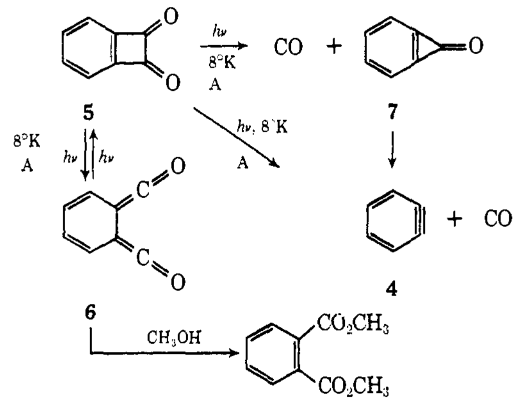
(8) H. A. Staab and J. Ipaktschi, *ibid.*, 483 (1966).

Scheme I



EPA at 77°K.[9] In the latter experiment, Kolc showed that biphenylene was formed when the matrix was warmed showing that benzyne was the decarbonylation product.[9] Irradiation of benzocyclobutenedione matrix isolated in argon at 8°K gives benzyne, carbon monoxide, and the bisketene (**6**, 2091 cm^{-1}) as primary products. The identity of the bisketene **6** was established by generating it in an argon–methanol matrix at 8°K and then warming the matrix and observing the concurrent disappearance of the infrared bands of **6** and the appearance of the dimethyl phthalate infrared spectrum. The observation of **6** supports the mechanism suggested by Staab and Ipaktschi[7] for the formation of dimers in the room temperature irradiation of **5**. In one experiment using acetone in the argon as an internal filter, a product with an 1838-cm^{-1} band was observed. This product decarbonylates to benzyne on irradiation and is tentatively identified as benzocyclopropenone (**7**). The formation of the bisketene **6** is photochemically reversible (Scheme II), and the ultimate yield of benzyne is quite high. Benzyne is reasonably stable photochemically, but it is slowly converted to acetylene.

Scheme II



Benzyne prepared from **1** and **5** shows bands at 1627, 1607, 1451, 1053, 1038, 849, 736, and 469 cm^{-1} (Figure 1). Warming the matrix containing benzyne to room temperature produces triphenylene (**8**, identified by the ultraviolet spectrum and parent ion, *m/e* 228) together with higher polymers. Direct evidence for the chemical identity of benzyne is provided by an experiment conducted in an argon matrix containing furan. In this experiment, the disappearance of benzyne infrared bands on warming to 50°K can be correlated with the appearance of the infrared bands of the benzyne–furan adduct **9**. This direct correlation of benzyne disappearance with the formation of the adduct leaves no room for doubt that the species under observation is benzyne.

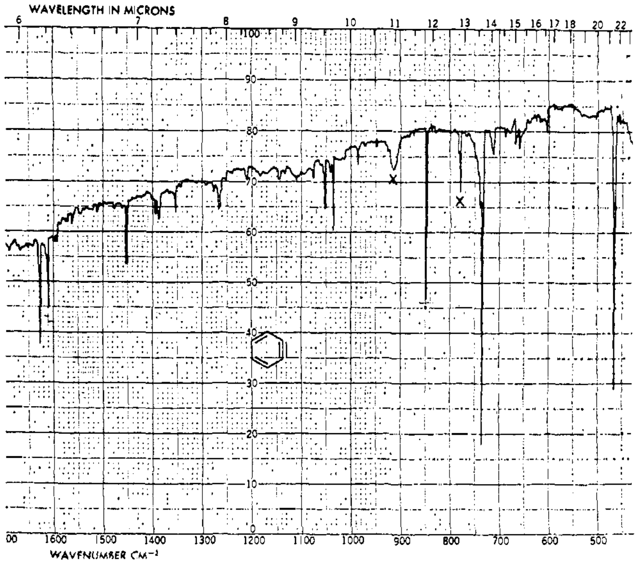
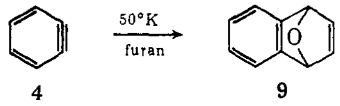
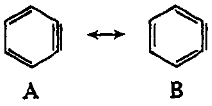


Figure 1. Infrared spectrum of benzyne (matrix isolated in argon at 8°K) prepared by irradiation of **5**. Bands at 1627, 1607, 1451, 1053, 1038, 849, 736, and 469 cm^{-1} are definitely benzyne bands. The bands marked with an × are definitely not benzyne bands.



The infrared spectrum of benzyne provides some insight to the structure of benzyne. The out-of-plane deformation modes are similar in pattern to benzenoid systems which have four adjacent hydrogens (*cf.* **1** and **5**) and the bands are shifted to lower frequency. This shift to lower frequency indicates a less rigid molecule with respect to out-of-plane distortion. Double and single carbon–carbon bond frequencies (1627, 1607, and 1451 cm^{-1}) are observed. This suggests that the molecule has more cyclohexatriene character as far as the π system is concerned. This is reasonable in terms of a shortened bond (the triple bond) which would tend to localize the π system. In terms of valence bond structures, this indicates that A is energetically favored with respect to B.



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