crystallization from cyclohexane gave white needles (86%), mp 95–96° (lit.[11] 97°).

In conclusion, the mild conditions, high yields, convenience, and absence of side products coupled with the superior and controllable selectivity recommend the reagent for synthetic applications which would not tolerate harsher reagents. Particularly attractive possibilities include the removal of iodo groups in the presence of carbonyls or the reduction of aldehydes selectively in the presence of ketones or halides.

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Molecular Beam Chemistry. Persistent Collision Complex in Reaction of Oxygen Atoms with Bromine Molecules

Sir:

Crossed-beam experiments have demonstrated that many reactions proceed *via* formation and decomposition of a "sticky" collision complex which persists for many vibrational periods and at least a few rotational periods, or typically $\gtrsim 5 \times 10^{-12}$ sec. Among the well-studied examples are reactions involving alkali halide salts,[1–3] reactions of halogen atoms with olefins,[4,5] and several ion–molecule reactions.[6,7] For each of these systems the intermediate complex could be reasonably postulated to be a stable molecular species which correlates with the ground-state reactants and products. This communication reports a study of the reaction

$$O(^3P) + Br_2(^1\Sigma_g^+) \longrightarrow BrO(^2\Pi) + Br(^2P)$$

It is found to go *via* a persistent collision complex with large reaction yield and no activation energy, but the known, stable Br_2O molecule does not correlate with the reactants.

Figure 1 shows the experimental results. The primary data comprise velocity distributions of BrO at seven scattering angles, obtained with an apparatus employing mass spectrometric detection and time-of-flight analysis.[8] The O beam comes from a rf discharge source; the Br_2 beam comes from a supersonic nozzle. The product velocity analysis makes possible a quantitative kinematic transformation of the laboratory data to determine the scattering distribution in the "center-of-mass" (CM) coordinate system.[8] This system pertains to an observer riding with the centroid of the three atoms and thus displays the relative motion of the reaction products.

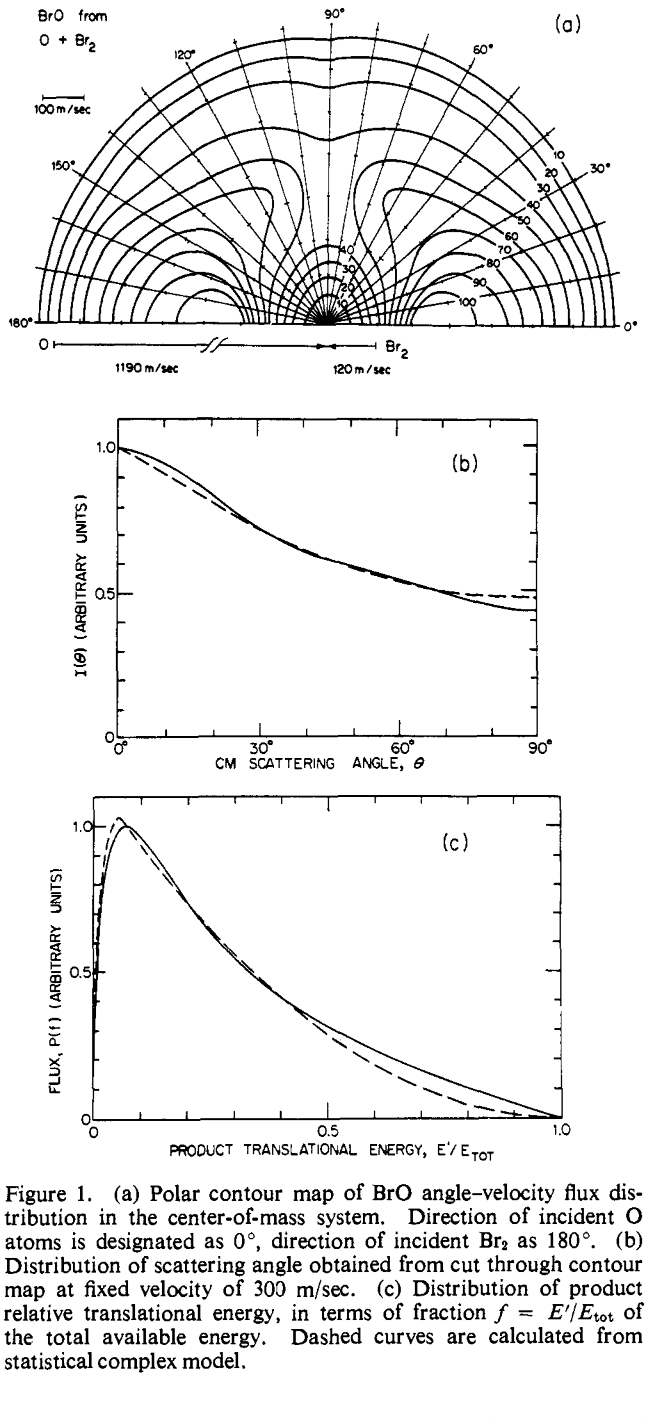

Figure 1. (a) Polar contour map of BrO angle–velocity flux distribution in the center-of-mass system. Direction of incident O atoms is designated as 0°, direction of incident Br_2 as 180°. (b) Distribution of scattering angle obtained from cut through contour map at fixed velocity of 300 m/sec. (c) Distribution of product relative translational energy, in terms of fraction $f = E'/E_{tot}$ of the total available energy. Dashed curves are calculated from statistical complex model.

In Figure 1, the CM distributions exemplify the properties expected for a persistent complex more accurately than any previously studied reaction. These properties include: forward–backward symmetry with respect to the initial relative velocity vector, velocity spectrum independent of scattering angle, and characteristic shapes of the angular distribution, $I(\theta)$, and relative translational energy distribution, $P(f)$. For comparison, Figure 1 includes curves calculated from a simple statistical model[1,9] akin to the RRKM theory of unimolecular decay.[10] According to the model, $I(\theta)$

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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 $(F\text{–}Cl\text{–}Cl)^+$ 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 $\bar{a}'\text{-}3\bar{\sigma}$ might cross the $\bar{a}''\text{-}3\bar{\pi}$ and $\bar{a}'\text{-}3\bar{\pi}$ 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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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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