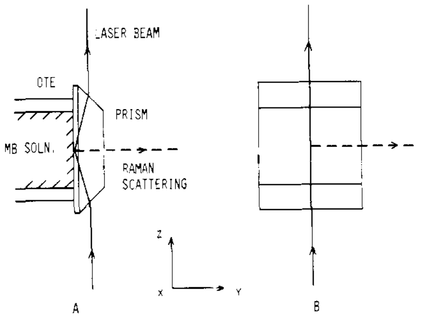

Figure 1. Raman cell for the internal reflection mode. The incident angle which depends on the geometry was ca. 74° and greater than the critical angle in the present geometry where the interface was parallel to the laser beam propagating in air (z axis). Raman scattering was observed in the direction along the y axis and perpendicular to the electrode surface (arrangement A) or perpendicular to the plane of incidence by rotating the cell 90° around the z axis (arrangement B). The electric vector of the incident laser beam was parallel to the interface in A and parallel to the plane of incidence in B.

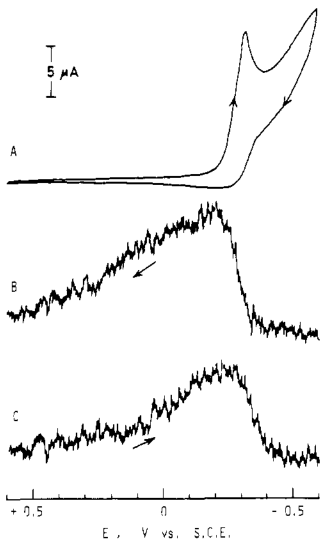

Figure 2. Current-potential curve (A) and the change in the internal reflection resonance Raman intensity at 1625 cm^{-1} of the adsorbed MB at SnO_2 electrode-aqueous solution interface as a function of the applied potential for the cyclic linear sweep mode (scan rate 4.8 mV s^{-1}) on anodic sweep (B) and on cathodic sweep (C). 1×10^{-4} M MB in 1×10^{-2} M aqueous KCl solution. Raman scattering was observed with the arrangement B in Figure 1.

1042, 1167, 1187, 1302, 1365, and 1472 cm^{-1}. The relative intensities of these bands were different from those observed in the spectrum excited at 488.0 nm. Observation of the internal reflection resonance Raman spectra of the adsorbed MB at the quartz-aqueous and at the SnO_2 electrode-aqueous solution interfaces in the wavenumber region less than 1250 cm^{-1} was not easy because of interference of the high background Raman scattering from quartz or glass substrate of OTE. Although the spectra obtained at both interfaces are very similar to that of solution, the observed spectra can be considered to be due to the adsorbed MB because of the presence of a negligibly slight amount of MB solute within the penetration depth compared with the adsorbed MB at the concentration measured.[3,18]

The change in Raman intensity at 1625 cm^{-1} of adsorbed MB as a function of the applied potential is shown in Figure 2 for the cyclic linear sweep mode. The internal reflection resonance Raman spectra of adsorbed MB disappeared as expected when the adsorbed MB was reduced to leuco-MB at more cathodic potential than −0.4 V vs. SCE. The decrease of the Raman intensity observed with increase of anodic potential can be interpreted by the decrease of the amount of adsorbed MB due to the repulsion of adsorbed MB cation with increasing positive charge of the electrode surface. This potential dependence of adsorption and the decrease of the amount of adsorbed MB due to the change in the surface charge with lowering pH of the aqueous solution in contact with the quartz surface have been confirmed previously[18,19] using IRS in the visible region.

In conclusion, Raman spectra of the adsorbed submonolayer at solid-solution interface were obtained without interference from species in bulk solution using internal reflection resonance Raman spectroscopy. Reabsorption of Raman scattering troublesome in resonance Raman spectroscopy can be neglected in this mode. This method can be applicable widely for the study of a variety of interfaces[20] in situ involving electrode-solution interfaces with OTE.

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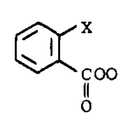
Direct Observation of a Sulfurane Intermediate in the Neighboring-Sulfide-Assisted Thermolysis of a Perester[1]

Sir

The anchimeric acceleration of O–O homolysis in perester **1a** in chlorobenzene at 60 °C amounts to a factor of 2.45×10^4 relative to **1b.**[2] Peresters **1c–f** and **2** also exhibit substantial rate enhancements mediated by neighboring group participation in reactions leading primarily to free radicals.[2-6]

In 1962, sulfurane **3** was postulated as a logical albeit unprecedented intermediate in the thermolysis of **1a.**[2] The recent



1a, X = SPh

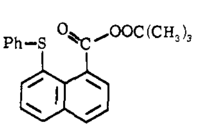
b, X = H

c, X = I

d, X = SMe

e, X = SOPh

f, X = CH=CPh$_2$



2

isolation of a stable sulfurane from decomposition of a bis perester,[1a] the discovery of similar reactions leading to hypervalent iodine species,[7,8] and the large body of recent work on sulfuranes,[9] especially work suggesting that **3** might be unusually stable by dint of its apical-equatorial five-membered ring,[10] led us to reexamine the decomposition of perester **1a.** We report herein strong support for the 1962 postulate.

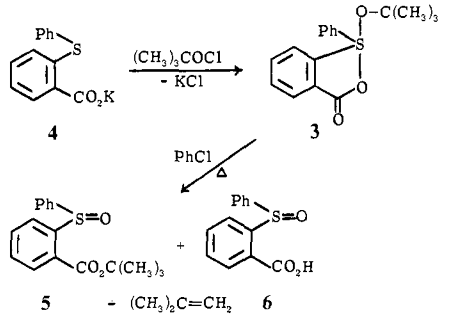
In addition to the expected peaks recording the first-order disappearance of perester **1a** ($k = 2.41 \times 10^{-3}$ s^{-1}; 70 °C in chlorobenzene) and the appearance of acetone and *tert*-butyl alcohol, an examination of the NMR spectrum of the reaction mixture at intermediate times shows a singlet at 1.21 ppm, tentatively assigned to sulfurane **3** (*tert*-butyl group) on the basis of two facts. (1) The signal grows to a maximum intensity after about 12 min at 70 °C corresponding to ca. 19% of the original intensity of **1a,** then decreases to zero. (2) The 1.21-ppm peak disappears completely, the *tert*-butyl alcohol peak increases in area, and all other peaks in the aliphatic C–H region are unchanged when a drop of D_2O is added to a reacting sample of **1a.** The tentative assignment was verified by synthesis and characterization of sulfurane **3.**

Reaction of a stirred suspension of potassium *o*-(phenylthio)benzoate, **4,** in dry CCl_4 with an equimolar amount of *tert*-butyl hypochlorite, added in one portion in an inert atmosphere glove box at ambient temperature, afforded, after filtration and addition of dry pentane to the filtrate, a white, crystalline, water-sensitive solid, **3:** ^{1}H NMR (100 MHz, C_6H_5Cl), 1.18 (s, C(CH_3) of **3**),[11] 1.15 ppm (s, $(CH_3)_3COH$ impurity from hydrolysis); ^{13}C NMR (15 MHz, $CDCl_3$), 28.9 ppm (s, CH_3) and 84.0 ppm (s, CMe_3); infrared ($CHCl_3$), 1640 cm^{-1}.[12]

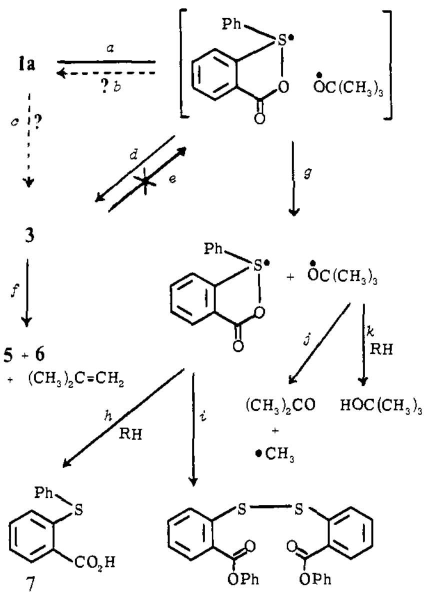
At 70 °C the ^{1}H NMR of a chlorobenzene solution of **3** shows the 1.18-ppm peak decaying in intensity and shifting progressively downfield to 1.21 ppm. New peaks arise at 1.61 (t, $J = 0.8$ Hz, isobutylene CH_3) and 1.41 ppm (s, *tert*-butyl group of ester **5**). Upon cooling, the solution deposits crystalline **6.**[13] Based on studies of sulfuranes analogous to **3,**[14] the observed products **6** and isobutylene are those expected from decomposition of **3.** Thus there is little doubt that the product of the reaction of **4** with *tert*-butyl hypochlorite is the desired sulfurane **3.** (See Scheme I.)

Evidence for the involvement of **3** in the pyrolysis of **1a** at 70 °C is seen in ^{1}H NMR, ^{13}C NMR, and infrared spectroscopic evidence for the presence of **3** at intermediate times and its absence from the final reaction mixture.

Scheme I



Scheme II



Decomposition of the isolated sulfurane **3** in chlorobenzene or in chlorobenzene containing products of decomposition of **1a** produces no detectable acetone (by NMR), nor any *tert*-butyl alcohol in excess of that present initially as the result of unavoidable hydrolysis. Both acetone and *tert*-butyl alcohol are major products of the decomposition of **1a,** and report the intermediacy of *tert*-butoxy radicals in the system. A reexamination of this product mixture shows, in addition to the previously reported[2] **6,** a minor amount of **5.** The reasons for the larger amounts (ca. 45%) of **5** formed in the decomposition of pure **3** will be discussed in a later paper.

These observations drastically contract the set of possible mechanistic descriptions of the anchimerically assisted decomposition of **1a.** One description which is consistent with these results is outlined in Scheme II.[15]

The absence of acetone, a product signature of the *tert*-butoxy radical, from among the decomposition products of **3** rules out path c—rapid rearrangement of **1a** to **3,** perhaps by an intramolecular biphilic insertion of sulfur into the O–O bond[16]—followed by rate-determining decomposition of **3** (paths e and f) as the sole mechanistic route to all products. Either step a is rate-determining, with the radical pair defining the watershed between radical- and sulfurane-type products or loss of **1a** occurs by the two competing routes a and c, **1a** itself being the branch point. This latter possibility is less likely, since the rate constant for loss of **1a** is linearly correlated with solvent polarity, while the fraction of scavengeable radicals from **1a** is entirely uncorrelated with solvent polarity.[3]

Several reasonable mechanisms detailing step f may be written; work directed at establishing the details of this heterolysis is in progress.

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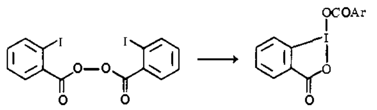

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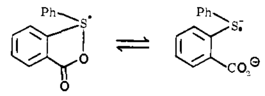

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Reactions of Magnesium Atoms with Cyclic Ketones

Sir:

In recent years the reactions of metal atoms with organic substrates, through the technique of codeposition at low temperatures, have been an active area of chemical research.[1]

We wish to report the first investigations of the reactions of ketones with metal atoms and to specifically focus on the reactions of magnesium atoms with cycloheptanone for reasons which will be made clear later in this communication. Although reactions of magnesium atoms with water, ammonia, and alkyl halides have been reported previously[2] and very reactive magnesium slurries have been prepared by this codeposition technique,[3] nowhere have the reactions of magnesium atoms with ketones been discussed. It should be pointed out at the outset that products from magnesium atom reactions with ketones reported herein are not found when clean finely divided bulk magnesium[3] is allowed to react with the same ketones; indeed, when this experiment was done only a trace of product, unlike that from the atom reactions, could be detected. A metal atom reactor similar to the one described by Skell and Wescott[4] but modified to use a resistively heated alumina crucible was used.

When magnesium is codeposited with cyclopentanone at 77 K we find, among the products, substantial amounts of cyclopentene and 1,1′-dihydroxydicyclopentyl. Similarly if one allows magnesium and cyclohexanone to react under these conditions substantial amounts of cyclohexene and 1,1′-dihydroxydicyclohexyl are produced.

The isolation of the olefinic products in these reactions, clearly indicating deoxygenation by the magnesium vapors, led us to suggest a carbene or carbenoid intermediate. Thermodynamic calculations based on bond energies and the heat of vaporization of magnesium oxide[5] suggest that the reaction of magnesium atoms with cyclic ketones to yield carbenacycloalkanes and magnesium oxide should be exothermic by at least 55 kcal mol^{-1}. The absence of a product resulting from a reaction unique to carbenes in the aforementioned reactions, however, pointed out the necessity of investigating another system which would yield data on this point.

Friedman and Schechter have reported on the thermolysis of diazocycloalkanes to yield carbenacycloalkanes.[6] In this work they have shown that carbenacyclopentane yields cyclopentene as the only product. Similarly carbenacyclohexane yields only cyclohexene but, on the other hand, carbenacycloheptane yields cycloheptene (82%) and norcarane (18%). The latter product, clearly, is the result of carbon–hydrogen insertion of the divalent carbon, a reaction which is unique to carbene or carbenoid species.

With this background we proceeded to investigate the reaction of atomic magnesium with cycloheptanone. The reaction is carried out using the usual codeposition technique with the reactor immersed in liquid nitrogen.[4] Approximately 200 mg of magnesium was vaporized in a typical run. Upon completion of the codeposition, the liquid nitrogen is removed, and any volatile products and unreacted substrate are pumped into a liquid nitrogen cooled trap from which they can subsequently be removed and analyzed by gas chromatography. The residue in the reactor is then taken up in ether and filtered from the insoluble material and the solution allowed to evaporate. The resulting oil is analyzed by high pressure liquid chromatography.

We have found that 13% of the magnesium vaporized can be accounted for as leading to 1,1′-dihydroxydicycloheptyl. Another 13% of the magnesium can be accounted for by the volatile hydrocarbon products. In addition there is considerable gray ether insoluble residue containing unreacted magnesium. Apparently a major portion of the magnesium repolymerizes, a result not uncommon in metal atom chemistry.[1]

Analysis of the volatile products shows that they consist of cycloheptene (91%), norcarane (5%), and cycloheptane (4%). The ether soluble nonvolatile oil contains 37% 1,1′-dihydroxydicycloheptyl, the balance being a mixture of aldol condensation products. The hydrocarbon products were identified by comparing their gc retention times (Carbowax 20 M and S. E. 30) and mass spectra to those of authentic samples. The 1,1′-dihydroxydicycloheptyl was identified by comparing its HPLC retention time (Corasil II, 60/40 volume/volume *n*-heptane/chloroform) to that of an authentic sample prepared according to the procedure of Greidinger and Ginsburg.[7] In addition, crystals were isolated from the oil (mp 76–78 °C, reported 78 °C) by adding cold *n*-hexane and allowing the solution to stand overnight at 5 °C. These crystals gave an IR spectrum identical with the authentic sample and when mixed with the authentic sample, caused no depression of its melting point.

The isolation of norcarane among the hydrocarbon products requires the intervention of a carbene or carbenoid species and the formation of cycloheptane suggests a certain amount of triplet carbenacycloheptane. Although the aldol condensation products were not individually isolated and identified, the oil, in addition to the 1,1′-dihydroxydicycloheptyl, shows a distribution of products by HPLC which bear a striking resemblance to the aldol condensation products obtained from cy-