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Isolation of HO₂ from the Hydrogen, **Oxygen Diffusion Flame***

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TECHNIQUE for the isolation and identification of intermediate species in diffusion flames has been described by Stadnik.1-3 Reactive products are absorbed in a film of water flowing close to the flame, and are later identified by appropriate analyses. In the case of the hydrogen, oxygen flame a reducing substance was isolated³ which reacted slowly with potassium permanganate, and after the permanganate titration, liberated large quantities of iodine from potassium iodide. Stadnik attributed this behavior to the presence of hydrogen peroxide and larger amounts of hydrogen superoxide, H2O4, resulting from the absorption of HO2 from the flame. A slow decomposition of the H2O4 to oxygen and hydrogen peroxide was believed to account for the analytical results.

Because of the importance of HO₂ in mechanisms proposed for various chain reactions involving hydrogen and oxygen, and the scarcity of direct experimental evidence for its existence, an attempt has been made to repeat and extend these experiments. The results indicate that nitrous acid from the oxidation of atmospheric nitrogen is present in the absorbing solutions, and that hydrogen peroxides are not present; it appears that the evidence attributed to hydrogen superoxide can be adequately explained in terms of nitrous acid.

An apparatus similar in design to that described in detail by Stadnik³ was used. The reaction vessel, a tin plated copper tube (130 mm long by 20 mm i.d.) is mounted vertically and equipped with shallow overflow dishes at the top and bottom. A sample of cool (15°C) water, recirculated by a small glass pump, pours continually down the inner walls of the tube. Oxygen enters the reaction zone through small perforations in the upper wall of the tube, and hydrogen is introduced through a 5 mm i.d. quartz tube mounted coaxially with the reaction tube; the flame burns at the hydrogen inlet and extends to within 2 mm of the flowing water surrounding it. In all experiments a 30 percent excess of oxygen was used; 400 cc of water was recirculated at a rate between 400 and 600 cc per minute, and 50 cc aliquots were analyzed after 0.8 to 1.0 moles of hydrogen had burned.

The recirculated solutions gave a positive test for nitrite in a modified form of the Griess-Illosvay method.⁴ When mixed with acidified titanium sulfate, the solutions failed to show the yellow color characteristic of the peroxytitanic complex.

The uv absorption spectrum of a recirculated solution showed increasing absorption below 2200A and a maximum in the vicinity of 3600A. The absorption near the visible corresponds to that reported for nitrous acid⁵ between 3100A and 3900A. No maximum in this region occurs in the spectrum of dilute aqueous hydrogen peroxide.

On titration with 0.01 N permanganate, the reactions were slow and the analyses less precise than corresponding titrations with ceric ion. The slow reaction with permanganate is characteristic of nitrous acid. After a permanent permanganate end point had been reached, the samples were freed of oxygen, treated with potassium iodide, and left overnight in sealed flasks; no iodine in excess of that corresponding to the permanganate blank was liberated. The large quantity of liberated iodine found by Stadnik could arise from a slight undertitration with permanganate (caused by slowness of the MnO4-, NO2- reaction) and incomplete removal of traces of oxygen from the sealed flasks, since nitrite is known to be an effective catalyst for the oxygen, iodide reaction.

The interfering nitrogen probably comes from the atmosphere around the apparatus, although 0.1 percent of nitrogen in the hydrogen or oxygen supplies if completely burned would be sufficient to cause these results. Addition of 3 percent nitrogen to the oxygen supply caused a fourfold increase in the nitrous acid concentration of the final solution. Saturating the water sample with nitrogen at 1 atmos served to increase the final nitrous acid concentration by about 30 percent.

Since nitrous acid would destroy any hydrogen peroxides that might be dissolved, this method will be inapplicable to the study of flame intermediates unless it is modified to insure exclusion of atmospheric nitrogen from the reaction.

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s-Triazine. IV. The Mass Spectrum

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***HE** mass spectrum of s-triazine has been obtained using a Consolidated Engineering Corporation, model 21-103-A mass spectrometer. A vapor sample of s-triazine, which is a solid with a vapor pressure of a few mm of mercury at room temperature, can be readily obtained after pumping out air at dry ice temperature. The spectrum obtained is shown in Table I, with formulas for the expected fragments at each mass.

TABLE I. Mass spectrum of s-triazine.

Mass/charge	Pattern (%)	Fragments
12	7.9	С
13	7.2	CH
14	2.1	N
24	2.0	$\overline{\mathbf{C}} - \mathbf{C}(R)$
25	1.6	$\tilde{C}H - \tilde{C}(R)$
26	6.4	Č-N
27	56.1	HC-N
28	83.3	(HC - N)H or $N - N(R)$
20	14	
38	51	$\dot{C} - N - C$
30	4 3	CH -N -C
40	2 2	CH -N -CH
41	0.5	N = CH = N
21	2.5	C = N = C = N
54	12.0	CHNC NOTCONCHN
33	10.9	
34	04.1	Cn = N = Cn = N
55	2,5	
81	100.0	CsN3H3
82	4.4	(1)

(R) = rearrangement; (I) = isotopic. Spectrum obtained at 270°C., 97.5 μ A ionizing current, low amplifier gain, metastable suppressor out, 70 volts ionizing potential, mass 58 recorded at 714 volts. Sensitivity of mass 81 in s-triazine =40.5 div./ μ . Sensitivity of mass 43 in butane =39.1 div./ μ ; butane pattern, 58/43 =12.5 percent, 29/43 =42.6 percent.

The mass spectrum of s-triazine is characterized by a large parent peak at mass 81, relatively large peaks corresponding to fragments of the C2N2 and CN groups, small peaks of C2N, CN2, C and N fragments, other small peaks due to rearrangements, and complete absence of C₂N₃ and C₃N₂ fragments. The spectrum differs from that of benzene in the greater importance of the CN and C2N2 fragments in s-triazine in comparison with the analogous C_2 and C_4 fragments in benzene, and in the absence of C_2N_3 and C₃N₂ fragments, while C₅ fragments are obtained in benzene.

The peaks at masses 24 and 25 are believed to be due, not to impurities, but to rearrangement. It is well known that rearrangement peaks are frequently encountered in mass spectra, particularly in compounds containing oxygen and nitrogen.¹⁻³ In some cases such peaks may be the largest in the spectrum.² However, the types of rearrangement which are commonly observed can be explained by rearrangements of hydrogen atoms and do not require any rearrangement in the skeleton of the molecule. The rearrangement peaks at masses 24 and 25 in s-triazine require a rearrangement in the skeleton of the molecule. The peak at mass 28 may be due to a hydrogen atom rearrangement to form CNH₂⁺ or to a skeleton rearrangement to form N2⁺. Other peaks may involve contributions from rearrangements even though the peak can be explained by the expected fragments formed without rearrangement; for example, mass 26 may be due in some part to $C_2H_2^+$.

It has been shown⁴ that the mass 26 peak in the benzene spectrum is due to a split into $CH = CH^+$ and 2CH = CH. If s-triazine splits analogously into 3 fragments instead of the usual 2 fragments, the appearance of $\check{C}-C$ fragments, which apparently requires the formation of at least 3 fragments, might not be too surprising. The distance between atoms in the potential C-Cbond in s-triazine is short enough so that a C-C bond can be formed⁵ without requiring change in the position of the C atoms, and thus appearance of C-C fragments does not violate the Franck-Condon principle.2,6 Stevenson7 has concluded from studies with C13 tagged propane and butanes that individual carbon atoms tend to lose their identity in the process of fragmentation on electron bombardment. However, because the stripped C-C fragment has a very low abundance in the propane and butane spectra, it was not possible to show that the rearrangement in C13 tagged propane and butane involved skeleton rearrangements. The evidence for skeleton rearrangements presented in this paper contributes further to the idea that the individual atoms lose their identity in the process of fragmentation.

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A Theoretical Study of the Colored Alkali Oxides

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HERE are three kinds of oxides, common to all the alkali metals: Me₂O, Me₂O₂, and MeO₂. Furthermore, the sesquioxides Me₄(O₂)₃ have been prepared from at least Rb and Cs. The crystal structures of all these oxides have been determined by Helms and Klemm.¹ The sesquioxides are characterized by a dark color, whereas the other oxides are almost colorless. This feature of the sesquioxides can hardly be attributed to any of the separate ions. Most probably, the color depends on the structure of the crystal lattice.

In the present study an attempt has been made to describe the electron distribution of the sesquioxides in terms of semilocalized orbitals. By means of this description an explanation of the dark color has been suggested.

The computations have been carried out using the parameters of the Rb4(O2)3 crystal, but analogous results could obviously be obtained in the case of $Cs_4(O_2)_3$.

We have considered an Rb atom and the three nearest O atoms, $O_{\alpha}, O_{\beta}, and O_{\gamma}, as an entity. Let \varphi_{Rb}, \varphi_{\alpha}, \varphi_{\beta}, and \varphi_{\gamma}$ be suitable atomic orbitals of Rb, $O_{\alpha}, O_{\beta}, and O_{\gamma}$. We have assumed that the valence electron of Rb can be assigned to an orbital:

$\varphi = a \varphi_{\rm Rb} + b (\varphi_{\alpha} + \varphi_{\beta} + \varphi_{\gamma}).$

The energy has been calculated from the expression

$$E = \int \varphi^* H \varphi d\tau,$$

where H is the Hamiltonian of the electron in the field from the whole crystal. The parameters a and b of φ have been determined by variation of E with respect to a and b. This computation has

TABLE I.

pprox.	a/b	E	ΔE	λ
I	0.3	-0.296 a.u.	0.07 a.u.	6500A
-	-5.7	-0.226 a.u.		
II				
	0.6	-0.314 a.u.	0.00 a.u.	1500A
11	0.6 -4.1	-0.314 a.u. -0.253 a.u.	0.06 a.u.	

been carried out using two different approximations of the potential energy. The results are collected in Table I. The column a/b shows that in the lower state the main contribution to φ comes from the oxygen orbitals, and in the higher state φ is almost a pure Rb orbital. The last two columns give the difference in energy ΔE between the two states and the corresponding wavelength λ , which is seen to belong to the visible part of the spectrum. Our suggestion is, therefore, that a transition between these two states gives rise to the color of the crystal.

Full details will be published by one of us (B. G.) in Arkiv för Fysik.

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Color Centers in Synthetic Quartz*

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R ECENTLY, Cohen¹ has reviewed some of the literature on the absorption maxima in fused and crystalline quartz. In particular, the work of Yokota,^{2,3} was discussed and some doubt indicated as to the reality of the absorption maximum reported by Yokota at 2.67 ev (462 m μ) in x-irradiated α quartz.

This note is written to report an absorption maximum in x-irradiated synthetic quartz at 2.64 ev (470 mµ). Samples of synthetic quartz cut perpendicular to the c axis were employed. The quartz used was cut from crystals grown by the Bell Telephone Laboratories, Inc., and by the Brush Development Company. Quartz from both sources yielded the 2.64 ev maximum when

