Identification of HO_2

from our Chemical Physics Correspondent

MOST chemists and chemical engineers would feel that HO_2 is one of the commoner and better known of the gas phase free radicals which are common intermediates in so many reactions. Hydrocarbon combustion, both in heating plants and in motor engines, is a major process in which HO_2 is a significant intermediate and many important kinetic rate constants are concerned with its creation and subsequent destruction. However clear cut, physical identification and study have proved remarkably difficult. Even the powerful tools of photolysis and of matrix isolation have found HO_2 to be a slippery customer and ultraviolet, infrared and electron resonance spectra of only indifferent quality and resolution have been obtained. More informative gas phase spectroscopy has been, hitherto, remarkably unsuccessful and this is not for want of much hard and difficult work.

Now, however, the powerful team of Radford, Evenson and Howard (*J. Chem. Phys.*, **60,** 3178; 1974) has obtained a remarkably clear spectrum which must be attributed to HO_2, unless even now this radical has sent a Doppelgänger to confuse us. The authors believe it relates to HO_2 but the evidence is indirect. The spectrum appears from more than twenty likely reaction mixtures including $O_2+C_2H_4$, $O_2+C_2H_2$, H_2O_2+F, $H+O_2$ and from discharges in water vapour. The spectrum near 130 cm^{-1} vanishes when the H is exchanged for D or ^{16}O by ^{18}O, but it remains unaltered when ^{13}C is used instead of ^{12}C in the reagents. The species is certainly paramagnetic, probably uncharged and seems to contain an odd number of nuclei like H with a spin of 1/2. The evidence is certainly sufficient to convince most readers, including your correspondent, but is not quite at the level of absence of all reasonable doubt that would be required by a murder jury. A particularly important aspect of the present spectrum is its availability as a monitor during the maximisation of the concentration of the concentration and life-time of the HO_2 in future experiments. This will be of interest to research workers in combustion and further details of the rotational spectrum will be eagerly awaited by astrophysicists who would seek HO_2 in interstellar gas by means of its microwave spectrum.

The spectrum was observed with a powerful technique which uses the absorption of the H_2O and D_2O laser lines near 119, 126 and 139 cm^{-1} (84, 79 and 72 μm). Since these lines do not coincide perfectly with the HO_2 absorption, the latter is modified by a magnetic field up to 2 T (20 k gauss) using the Zeeman effect. This technique, called laser magnetic resonance, is sensitive only to paramagnetic species, so that the many diamagnetic species in the reaction stream do not interfere. Using magnetic field modulation and a phase sensitive detection system about twenty lines are easily detected with each laser frequency using separately the laser electric field parallel and perpendicular to the magnetic field, a change which modifies the selection rule on the Zeeman sublevels. Indeed the signal to noise ratio is such that the doublet nature of the lines, due to the proton magnetic moment coupling with the unpaired electron, is clearly resolved with a separation of 1 mT (10 gauss). The radical is close to a prolate symmetric top and has $A\sim 19.4$ cm^{-1} and $(B+C)/2\sim 1.26$ cm^{-1}. The rotational quantum numbers N and K provide useful state labels and the transition near 139 cm^{-1} is assigned to the K $3\leftarrow 2$ and N $19\leftarrow 18$ transition although N $20\leftarrow 19$ is not completely excluded by the evidence. There is a zero field splitting between the $J=N+1/2$ and the $J=N-1/2$ states which is 0.605 cm^{-1} for $K=2$ and 1.139 cm^{-1} for the $K=3$ level. The transitions are for the $J=N+1/2$ states.

Vegetation disturbance in arctic tundra

from Peter D. Moore
Plant Ecology Correspondent

THE slow recovery rate of alpine tundra following the disturbance of surface vegetation (see *Nature,* **249,** 690; 1974) is causing concern. A similar, but more complex problem confronts conservationists in arctic tundra regions, where the existence of permafrost within the soil means that thermal equilibrium is a critical factor in determining ecosystem stability.

Dingman and Koutz (*Arctic Alpine Res.,* **6,** 37; 1974) have studied the pattern of frozen subsoil distribution in a region of central Alaska where permafrost is discontinuous. They were concerned in particular with microtopography and the way in which such factors as aspect can influence the net potential radiation input and hence the depth of the active layer (seasonal thaw zone). A rather rough, non-linear correlation emerges between their potential insolation index and active layer depth, and their figures suggest that permafrost occurs where the average annual solar radiation falls below 265 cal cm^{-2} d^{-1}.

The anomalous points on the graphs of Dingman and Koutz, which distort some of their regressions, frequently correspond to locations of unusual vegetation type, such as forest cover or exceptionally thick moss hummocks. Evidently the influence of surface vegetation on ecosystem energy balance, particularly on albedo and on latent heat losses associated with transpiration, must be taken into account.

This aspect has been studied by Haag and Bliss (*J. appl. Ecol.,* **11,** 355; 1974) who have conducted experiments to test the effect of vegetation disturbance upon tundra energy budgets. Damage to surface vegetation and peat on areas used as roads during the winter months resulted in increased surface moisture and therefore in considerable albedo changes (6.1%, compared with 15.2% in control sites); in consequence there was an increase in net radiation input in the road site. In addition, the compaction or disturbance of the surface peat layer led to an increase in thermal diffusivity, as a result of which higher soil temperatures were recorded during the day even at a depth of 50 cm in the road profile. Latent heat losses were greater in the control site, especially in the growing season when actively transpiring vegetation was fully developed and deeper reserves of water were being tapped.

One of the important conclusions of this work is that the use of tundra as a winter road alters the soil thermal régime, resulting in a deeper active layer in summer (about 56 cm compared with 36 cm in control). Similarly other types of disturbance such as fire and oil spills produced deeper active layers (46 cm and 42 cm respectively). Such conditions are conducive to surface instability and erosion. A possible solution to the problem would be the reseeding of disturbed areas to assist surface healing.

Wein and MacLean (*Can. J. Bot.,* **51,** 2509; 1973) investigated the potential of *Eriophorum vaginatum* (cotton sedge) as a recolonist of bare peat and mineral soil and came to the conclusion that the species could be of particular value where mineral soils were exposed and where the soil is permanently saturated. This is precisely the set of conditions found on parts of the winter roads. The seeds germinated best at 25–30° C and had no dormancy problems; when sown in July they were found to be strong enough to withstand the subsequent winter.

Reseeding experiments in disturbed tundra areas are now being conducted, but the initial data of Haag and Bliss suggest that the development of a vegetation cover will be slow; only 20–50% surface cover has been attained after three seasons' growth. Albedo has risen in the reseeded plots, leading to a decrease in the net radiation input, but active layer depth has decreased by only 2 cm (from 52 cm to 50 cm). It would seem that the loss of thermal insulation provided by a peat cover is even more vital for the maintenance of a shallow active layer than is high albedo. The redevelopment of a peat blanket will obviously take a very long time.