

Dielectric absorption at 20° C. in quinol crystallized from water

Evidence that structural breakdown of quinol does occur on grinding was obtained by previous workers4, who found that sulphur dioxide trapped in the quinol crystal lattice is partially liberated by grinding

The large dielectric absorption of quinol crystallized from water was accompanied by appreciable direct-current conductivity. This was also observed in the samples obtained from ethanol and methanol respectively. Quinol crystallized from methanol gave an initial conductivity about 5,000 times larger than that of the other samples. This may be related to its different structure and composition². It is less compact, and its crystal lattice contains entrapped methanol molecules which would escape on grinding and possibly take part in hydrogen-bond chain formation. High direct current conductivity has been reported by previous workers with other hydrogen-bonded structures, and is considered to be due to combined proton transition and dipole rotation⁵.

The sample disks were measured between mercury electrodes. Bridge methods were used at frequencies greater than 1 c./s. At lower frequencies the dielectric loss factor was calculated from the anomalous charging current measured at different times after the application of a D.C. potential⁶.

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¹ Meakins, R. J., and Sack, R. A., Aust. J. Sci. Res., 4, No. 2, 213 (1951).

* Palin, D. E., and Powell, H. M., J. Chem. Soc., 208 (1947).

^a Meakins, R. J., and Mulley, J. W., Aust. J. Sci. Res., 4, No. 3, 365 (1951).

⁴ Powell, H. M., J. Chem. Soc., 61 (1948).

⁵ Stearn, A. E., and Eyring, H., J. Chem. Phys., 5, 113 (1937). ⁶ Hamon, B. V. (in the press).

Spectra of Flames burning with Oxides of Nitrogen

WE have taken spectrograms of pre-mixed gas flames of hydrogen, ammonia, carbon monoxide and hydrocarbons burning with nitrous oxide, nitric oxide and nitrogen dioxide, respectively. The overall spectra of the hydrocarbon flames are very similar. CH-, CN-, NH- and OH-bands are present, and so also are the C₂-bands. The latter are quite strong

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in many flames (especially acetylene), but are generally weaker than the C2-bands in hydrocarbon oxygen flames. We found no evidence of the COfourth positive bands in any of these flames, however strongly our plates were exposed. This band system was reported by Behrens and Rössler¹ in a benz-ene – nitric oxide flame. In the region of the spectrum where this band system of CO should occur, we obtained strong NO-y-bands.

The flames of hydrocarbons burning with nitrogen dioxide have a double inner cone. The first inner cone emits a continuum of yellow light, and the second, which is separated from the first by a dark space, emits blue light containing C2-, CH-, CN-, NH-, OH- and NO-bands. In absorption spectra, the NO₂bands disappear in front of the first inner cone, and if benzene is taken as the fuel, the ultra-violet bands of benzene disappear at the same position as the NO_2 -bands. $NO_{-\gamma}$ -bands appear in absorption in the first inner cone and disappear again in front of the second inner cone. There is no doubt that both nitrogen dioxide and benzene decompose in the first inner cone. Some interaction between them also occurs, as it is possible to adjust the flame in such a way that the second inner cone blows off and the first cone burns alone, though with diminished flame velocity. Under these conditions a large amount of nitric oxide can be detected in absorption in the exhaust gases. This is normally consumed in the second inner cone.

The hydrogen - nitrogen dioxide flame has only one inner cone, and burns more rapidly than a saturated hydrocarbon flame with nitrogen dioxide. It seems that the nitrogen dioxide readily decomposes in the flame, and that the subsequent reaction of hydrogen and oxygen is sufficient to account for the high flame velocity. Nitric oxide does not seem to participate in the reaction, and consequently the flame does not reach its theoretical temperature. This is confirmed by various observations; for example, the OH-emission from the inter-conal gas is only about one-hundredth of that of a hydrogen/oxygen flame.

The hydrogen – nitric oxide flame has a very low speed, although it has a higher temperature than the hydrogen - oxygen flame, which is very fast. Thermal decomposition of nitric oxide is probably the ratedetermining process. This decomposition is very slow and will only take place at very high temperatures. The process is feasible in the hydrogen – nitric oxide flame because the velocity is low and sufficient time is available.

In contrast to the hydrogen flame, the ammonia nitric oxide flame burns readily and with a greatly increased flame speed. Strong NH-bands are emitted which scarcely appear in the spectra of the hydrogen flame. The presence of this radical may be re-sponsible for the different behaviour of the ammonia flame. NH-radicals may be able to decompose nitric oxide and provide an alternative path of low activation energy for the production of oxygen. Hydrocarbon - nitric oxide flames have velocities which increase in the same order as the increasing C_{2} -, CHand NH-band strengths, and it seems that nitric oxide again decomposes by radical reactions.

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¹ Behrens, H., and Rössler, F., Naturwiss., 36, 218 (1949).