Electronic Absorption Spectrum of the CH_3O-radical

IN flash photolysis experiments involving methyl nitrite, transient absorption bands at 1999, 2036 and 2064 Å were seen[1] faintly at 50 μsec, increasing in intensity slowly to a maximum at 2·5 msec and almost disappearing by 25 msec. These bands did not appear for any other nitrite tested. The reasons[1] for these bands being attributed to $CH_3O\cdot$ (being produced originally in a metastable excited state) were that this free radical, together with $NO\cdot$, was expected to result from the alkyl nitrites which are in fact accepted sources of $RO\cdot$ (despite the early investigations[2] in which the primary photochemical process in CH_3ONO was deduced to be dissociation to the molecules HNO and H_2CO), the observation of the expected partner fragment NO at the smallest delay times (50 μsec), and the virtual elimination of HNO, HCO, and formaldehyde in an excited state as the appropriate carrier.

Because methoxyl is the first alkyl homologue of hydroxyl, a consideration of the known electronic structure and transitions of the latter may be pertinent to a discussion of the possible transitions for $CH_3O\cdot$, as the replacement of the hydrogen atom by the methyl group (being completely saturated, with no easily excited electrons) should act only as a small perturbation of the electronic energy-levels resulting from hyperconjugation effects. The ground state of $\cdot OH$ is $^2\Pi$ and the first transition observed in absorption is to the $^2\Sigma^+$ state near 3100 Å. The transition may be described as one in which the unpaired electron in the $2p\pi$ orbital in the ground state is promoted to the σ^* anti-bonding molecular orbital in the $^2\Sigma^+$ state, consistent with the 20 per cent decrease of the vibrational interval in the upper state. The $^4\Sigma^+$ state in which there is one electron in each of the $2p\sigma$ and two $2p\pi$ orbitals would be the most probable low-lying metastable state. By analogy then, the methoxyl radical would also have an allowed transition to a level about 4 eV above the ground state in which the C—O stretching frequency should be distinctly smaller than the value of 1,050 cm^{-1} common for this vibration in infra-red spectra of methoxyl-containing compounds. This vibration should be readily excited in the upper state, making a progression in this vibrational interval observable, because of the increase in bond-length accompanying the occupancy of the anti-bonding orbital. In fact the observed frequency difference of approximately 800 cm^{-1} is fully consistent with the predicted spectrum, but the electronic transition itself lies at 6·3 eV, far above the corresponding $\cdot OH$ state. The vibrational interval of 800 cm^{-1} is also common as a bond-stretching frequency of first-row atoms, so that the coincidence with the theoretical prediction may be entirely fortuitous.

The energy absorbed at the maximum of the 2200 Å continuum of methyl nitrite is about 130 kcal/mole, sufficient to leave less than 90 kcal/mole to the methoxyl radical as excess electronic, vibrational and kinetic energy, after the N—O single bond is broken (36 kcal/mole (ref. 3) required) and the nitric oxide molecule may well have a small amount of vibrational excitation in the ground state (5 kcal/mole). Although there might well exist a state of $CH_3O\cdot$ similar to the $^4\Sigma^+$ state of $OH\cdot$ and lying less than 90 kcal/mole or 4 eV above the ground state, there is no reason to believe that the methoxyl radical can be formed in such a state because only a single σ-bond between N and O atoms is broken in the dissociation process. Thus $CH_3O\cdot$ would be formed in either a vibrationally or an electronically excited doublet state; if conversion to the metastable state were readily possible by some obscure mechanism, then the reverse reaction would also occur, and the life-time of the metastable state would not be nearly so great as 2·5 msec.

Following the previous assignment of these bands, the deduction was drawn[1] that the radical is reasonably stable under the conditions of temperature and pressure used. However, published kinetic investigations of methoxyl radicals have demonstrated[4] that there is only a small activation energy required for abstraction by methoxyl radicals, and further that there is no activation energy for disproportionation between methoxyl radicals to form methanol and formaldehyde. In other words, methoxyl radicals ought to destroy one another very efficiently, at every collision (apart from a possible steric factor). Again the analogy of hydroxyl proves illuminating: in the flash photolysis of water the hydroxyl radical lasts about 200 μsec (ref. 5) in the presence of only water or inert gases; if other hydrogen-containing gases are present the life-time is drastically reduced because of abstraction reactions. In fact this abstracting property of hydroxyl radicals has often been used[6] to prepare other radicals trapped in low-temperature solutions. Therefore, for methoxyl radicals to last 100 times as long as hydroxyl radicals under similar experimental conditions is exceedingly difficult to reconcile with available experimental evidence.

In summary, both spectroscopic arguments based on the position or the duration of the new bands and kinetic inferences fail to support the assignment of the transient spectrum near 2000 Å (ref. 1) to the methoxyl radical, or indeed to any other small radical. The time duration definitely points to the carrier being a relatively stable molecule with a singlet ground state, HNO and CS being simple instances of this type of chemical entity.

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Equation of State of Liquid-vapour Equilibrium with the Same Constants for Both Phases

As is known, the general equation of state of van der Waals, published in the year 1873, as well as its numerous modifications, expresses the relation between pressure, volume and temperature of gases-vapours and liquids qualitatively well, but generally only with a rather rough approximation with the same constants for both phases, especially for the liquid phase. Nevertheless, in view of the average experiences with these equations, several of their results, relatively, could be considered as accurate or satisfactory ones. Recent comparative calculations of Shah and Thodos[1] about the most common fourteen equations of state, based on the critical data of argon and *n*-butane, clearly confirmed anew these circumstances. They have found the formula of Redlich and Kwong[2] as the relatively best one by stating that " . . . this simple equation possesses the remarkable ability to represent the gaseous and liquid regions rather accurately"; yet they give no detailed results for the liquid states. Ree[3], somewhat earlier, reached a similar conclusion that " . . . the Berthelot equation of state[4] gives satisfactory results of liquid and vapour volumes in the vapour–liquid equilibrium for Ar, Kr, Xe, N_2, O_2, CO and CH_4, . . . ", that is, they examined definitely only the volume values.

It has been recognized for a long time that the best agreements can be reached for states of low up to medium densities, where the volume dependence of pressure is not so abrupt. Incomparably more delicate is the situation at greater densities and especially for the liquid state well below the critical point, where relatively slight volume variations correspond to relatively great pressure changes. Wohl[5], himself author of a well-known