

The Formation of Electronically Excited Oxygen in the Carbon Monoxide Flame

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both *R* and *P* branches, the intensity maximum in the *R* branch being quite near the head of the band. Many additional lines are therefore observed in both branches of the previously known bands. The head of the (1-1) band is observed in emission at $\lambda = 7683.8\text{\AA}$, while in absorption no lines of this band were observed below 7685.7 \AA , probably because of their low intensity.

We have found no evidence of any radiation from the CO_2 molecule, although careful search was made in the interval 7500-8800 \AA , where some of the CO_2 bands are expected to lie.⁷

In conclusion, the writers wish to call attention to the note of K. J. Laidler which appears in this issue. From theoretical considerations alone, he concludes that the combustion process of CO and O_2 may produce oxygen molecules in either the $^3\Sigma_u^+$ or $^1\Sigma_g^+$ states. Transitions from $^3\Sigma_u^+$ to the ground state $^3\Sigma_g^-$ produce the Schumann-Runge bands and transitions from $^1\Sigma_g^+$ to the ground state yield the currently observed bands.

* The work described in this paper was supported by the Bureau of Ordnance, U. S. Navy, under Contract NOrd-7386.

¹ George A. Hornbeck, J. Chem. Phys. **16**, 845 (1948).

² George A. Hornbeck, J. Chem. Phys. **16**, 1005 (1948).

³ G. H. Dieke and H. D. Babcock, Proc. Nat. Acad. Sci. **13**, 670 (1927).

⁴ W. Ossenbrüggen, Zeits. f. Physik **49**, 167 (1928).

⁵ R. Mecke and W. Baumann, Zeits. f. Physik **73**, 139 (1932).

⁶ R. S. Mulliken, Phys. Rev. **32**, 880 (1928).

⁷ D. M. Dennison, Rev. Mod. Phys. **12**, 175 (1940).

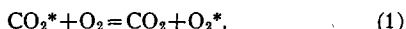
The Formation of Electronically Excited Oxygen in the Carbon Monoxide Flame

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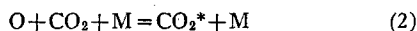
December 22, 1948

THE possibility of the formation of electronically excited oxygen in the carbon monoxide flame, by various processes that may be represented by



has been considered in a paper¹ presented at the Third Symposium on Combustion, Flame, and Explosion Phenomena in September, 1948. At the time there was no experimental evidence for such excitation of oxygen, but bands corresponding to two transitions from excited states have now been discovered, and were described in the previous letter.² It seems worth while, therefore, to present a more detailed discussion of this type of excitation.

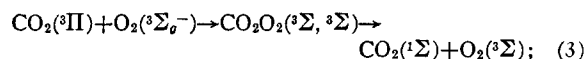
The carbon monoxide flame is known to contain oxygen atoms, which were detected by Gaydon³ using his nitric oxide method. The luminescence of the flame was previously thought⁴ to be due to the formation of electronically excited carbon dioxide by the process



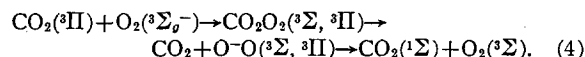
where M represents a third body; that excitation occurs in this process is necessary for conservation of spin angular momentum. The more recent discovery⁵ that the luminescence is due largely, if not entirely, to radiation by excited oxygen, calls for an explanation of the formation of these

molecules. The possibility of their formation by oxygen atom combination, analogous to the radical-radical reactions postulated⁶ to explain the formation⁶ of excited formaldehyde in hydrocarbon flames, is here excluded by the high quantum yield⁴ which indicates that one excited oxygen molecule is formed for about every hundred product molecules. This hypothesis is also eliminated by its failure to explain the disappearance of excited carbon dioxide molecules, which we know from direct evidence⁷ to be formed by reaction (2).

These facts seem to point directly to reaction (1) as responsible for the electronic excitation of oxygen. Excited carbon dioxide is in a triplet (probably a $^3\Pi$) state, and its interaction with a $^3\Sigma_g^-$ oxygen molecule will give $^1\Sigma^-$, $^1\Pi^-$, $^3\Sigma^-$, $^3\Pi^-$, $^5\Sigma^-$, and $^5\Pi^-$ states of the collision complex. Of these the triplet states will correlate with $\text{CO}_2(^1\Sigma) + \text{O}_2(^3\Sigma)$, which, therefore, can be formed without a violation of the spin-conservation rule; the process could be represented as

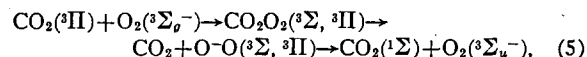


however, consideration of the form of the potential-energy surfaces suggests that ionic surfaces are also involved, viz.



This scheme would account for the production of several triplet states of oxygen. However, formation of the lowest ($^3\Sigma_g^-$) state seems unlikely, since the ionic surfaces do not fall low enough; this would correspond to physical quenching, the energy passing into vibrational, rotational, and translational energy.

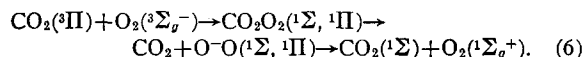
The production of oxygen in the $^3\Sigma_u^-$ state, which accounts for the Schumann-Runge bands which are formed by the transition $^3\Sigma_u^- \rightarrow ^3\Sigma_g^-$, seems much more probable from the standpoint of the smoothness with which the reaction can occur. The process may be represented as



assuming the ionic complex to be formed. However, an important question raised by the observation of these bands is an energetic one, since the reaction must certainly be endothermic. Reaction (2) is exothermic by (126.7-*E*) kcal. where *E* is the energy of excitation of the carbon dioxide in its 3Π -state; the energy of activation for the process⁷ is about 2 kcal., so that *E* cannot be greater than about 129 kcal. However, the energy of excitation of $\text{O}_2(^3\Sigma_u^-)$ is about 140 kcal., so that reaction (5) must be endothermic by at least 11 kcal., and therefore have an activation energy of at least this amount. If the flame temperature is about 3000°K, as seems to be the case, an activation energy of 15 kcal. would correspond to reaction occurring in one in about every 12 collisions, assuming no steric restrictions to reaction. Since the transition $\text{CO}_2(^3\Pi) \rightarrow \text{CO}_2(^1\Sigma) + h\nu$ is "forbidden," the radiative life of $\text{CO}_2(^3\Pi)$ may well be long enough for a large fraction of the $\text{CO}_2(^3\Pi)$ molecules to effect the required number of collisions with O_2 and hence transfer their electronic energy. Thus the production of the Schumann-Runge bands, which

at first sight seemed surprising, appears on further discussion to involve no theoretical difficulties; the detailed treatment of the mechanisms of such reactions involving a transfer of electronic energy still needs to be carried out, however.

In addition to the formation of $O_2(^3\Sigma_u^-)$ and $O_2(^3\Sigma_g^-)$ (lowest state), the production of $O_2(^3\Sigma_u^+)$ is possible. Reaction to give oxygen in a singlet state, e.g., $^1\Sigma_g^+$, can, as previously pointed out, proceed on singlet surfaces:



The production² of this state is probably to be explained by this reaction.

It may be noted in conclusion that the fact that most of the energy goes into the upper $^3\Sigma_u^-$ -state, in spite of the endothermicity of the reaction, is a further indication⁸ that in processes of this kind transitions are strongly

favoured which involve the transfer of a minimum amount of energy into non-electronic forms. This may be partly because of the large amount of resonance energy, but in this case perhaps more owing to the fact that the ionic states for the intermediate complex do not lie low enough to permit the formation of oxygen in lower electronic states.

¹ V. F. Griffing and K. J. Laidler, *Third Symposium on Combustion, Flame and Explosion Phenomena* (Madison 1948) (Williams and Wilkins, Baltimore, to be published).

² R. C. Herman, H. S. Hopfield, G. A. Hornbeck, and S. Silverman, *J. Chem. Phys.* **17**, 220 (1949).

³ A. G. Gaydon, *Proc. Roy. Soc. A* **183**, 111 (1944); *Trans. Faraday Soc.* **42**, 292 (1946).

⁴ Cf. V. Konratjew, *Zeits. f. Physik* **63**, 322 (1930); A. Fowler and A. G. Gaydon, *Proc. Roy. Soc. A* **142**, 362 (1933); A. G. Gaydon, *Spectroscopy and Combustion Theory* (Chapman and Hall, Ltd., London, 1942), Chapter VI.

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⁶ Day and R. N. Pease, *J. Am. Chem. Soc.* **62**, 2234 (1940); Topps and D. T. A. Townend, *Trans. Faraday Soc.* **42**, 345 (1946).

⁷ W. F. Jackson, *J. Am. Soc.* **56**, 2631 (1934); W. Groth, *Zeits. f. physik. Chemie* **B37**, 307 (1937).

⁸ Cf. K. J. Laidler, *J. Chem. Phys.* **15**, 712 (1947).