

Chemiluminescence during the Catalysis of Carbon Monoxide Oxidation on a Thoria Surface

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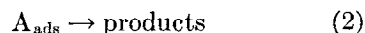
Received January 17, 1976; revised August 2, 1976

It is shown that the catalysis of carbon monoxide oxidation on a thoria surface treated in oxygen and *in vacuo* is accompanied by a specific luminescence. The luminous intensity is proportional to the catalysis rate and its spectral composition is different from that of oxygen adsorboluminescence on the same surface. When the thoria surface has undergone a pretreatment with hydrogen, this chemiluminescence is no longer observed. These results are interpreted in view of previous findings concerning the catalytic mechanism, and explained by the emission of light due to the annihilation of an exciton formed during the reaction of neighboring CO⁺ and O⁻ species.

INTRODUCTION

Emission of chemiluminescence during adsorption has been termed "adsorboluminescence" by the authors who discovered the phenomenon (1). It has lately been studied extensively in our laboratories (2-6). The question then arises whether such a light emission can occur during the course of a catalysis. Such an emission (which could perhaps be named "cataluminescence") seems to have been recognized only once (7) in the case of hydrogen oxidation on NiO-MgO solid solutions. Our own attempts (8) to detect a chemiluminescence due to catalysis during N₂O decomposition on thoria surfaces have failed, since the observed luminescence presents all the characteristics of oxygen adsorboluminescence.

More generally, as adsorption is an intermediate step in any catalysis, interference of adsorboluminescence should be avoided if light emission due to catalysis proper is sought. This can be accounted for by considering the simplified sequence:



depicted by Fig. 1, and where Eq. (2) is considered to be the rate determining step. If the sole adsorption step (1), of rate r_1 , is accompanied by a light emission, the intensity I_1 of which is assumed to be proportional to r_1 :

$$I_1 = \varphi_1 r_1, \quad (1)$$

we shall have a case of adsorboluminescence, in which light intensity will be pro-

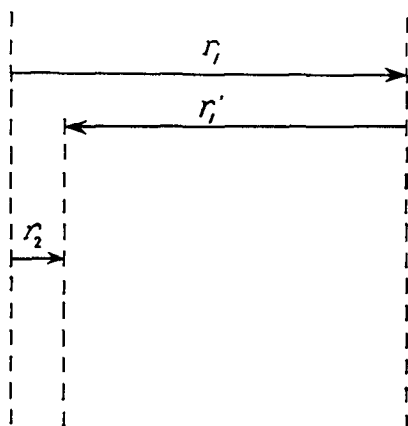


FIG. 1. Diagrammatic representation of the reaction rates of a two-step sequence (9): r_1 , rate of adsorption, r_1' , rate of desorption, r_2 , rate of surface reaction.

portional to the adsorption rate (here, greater than the catalysis rate), and the spectral composition will be identical with that observed during adsorption alone. On the contrary, if the rate determining step (2) is light emitting, with an intensity proportional to its rate, i.e., to the catalysis rate:

$$I_2 = \varphi_2 r_2, \quad (2)$$

then, the relationship (2) must be experimentally checked. Moreover, the spectral composition of the emitted light may have distinctive features.

In the following, we shall take this distinction as a guide, although the above example, considered for the sake of simplicity, may in fact be subject to complications: for instance, both steps (1) and (2)

may be radiative, or the radiative step may be subsequent to (2), and run at a rate which is not the catalysis rate, etc. The only catalytic system which will be considered in the following is the oxidation of CO on undoped thorium dioxide (thoria).

EXPERIMENTAL METHODS

1. Materials

Thoria has been obtained by thermal decomposition of thorium oxalate, according to a procedure described previously (10). As ample evidence has already shown (10), pretreatment is a major factor influencing surface properties. Table 1 summarizes the preliminary operations we made in order to obtain reproducible samples of thoria "A" and "B." The gases were used as supplied by the manufacturer (L'Air Liquide) and had a total impurity content not exceeding 10 vol/million.

2. Apparatus for the Study of Catalysis

Three different set-ups have been used, in which it was possible to determine *simultaneously* the catalysis rate and the luminous intensity. The first two were batch reactors provided with a recirculation loop. In one of them, a liquid nitrogen trap enabled the reaction product to be condensed, and in the other one no liquid nitrogen trap was used, but the gases were circulated by a glass pump (11). The pressure drop was continuously monitored in the first set-up by a mercury manometer equipped

TABLE 1
Thoria Surface Pretreatment

Operation sequence	Ambient conditions	Pressure (N m ⁻²)	Temperature (°C)	Duration (hours)	Solid obtained
1	Vacuum	1.33×10^{-3}			
2	Oxygen	213×10^2	450	4	
3	Vacuum	1.33×10^{-3}	450	16	Thoria A
4	Hydrogen	267×10^2	450	5	
5	Vacuum	1.33×10^{-3}	450	16	Thoria B

with a photocell which automatically followed the meniscus height variations, and in the second by a membrane differential pressure sensor A.C.B. Schlumberger 262 H. The third set-up was a differential flow reactor at the exit of which the CO_2 content was continuously monitored with an infrared absorption analyzer (Elliott Automation Junkalor Infralyt III).

In all three cases, the apparent catalyst surface was observed with a S.20 spectral response photomultiplier (the sensitivity of which falls to zero at 900 nm) followed by an amplifier and a recorder. In cases where light emission was too weak, a photon counting technique was used, with the same photomultiplier, followed by an amplifier discriminator (Model 1120 SSR Instru-

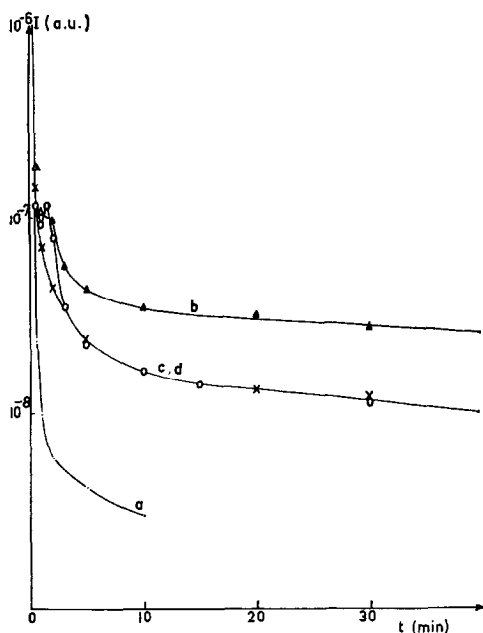


FIG. 2. Semilogarithmic representation of intensity (in arbitrary units) vs time during luminescence on ThO_2 "A." (a) Admission of oxygen alone, $P_0 = 47 \times 10^2 \text{ N m}^{-2}$, $T = 328^\circ\text{C}$; (b) mixture $6 \text{ CO} + \text{O}_2$, $P_0 = 313 \times 10^2 \text{ N m}^{-2}$, $T = 326^\circ\text{C}$, $r_0 \approx 1.33 \times 10^2 \text{ N m}^{-2} \text{ min}^{-1}$; (c) mixture $6 \text{ CO} + \text{O}_2$, $P_0 = 313 \times 10^2 \text{ N m}^{-2}$, $T = 308^\circ\text{C}$, $r_0 \approx 0.93 \times 10^2 \text{ N m}^{-2} \text{ min}^{-1}$; (d) mixture $2 \text{ CO} + \text{O}_2$, $P_0 = 135 \times 10^2 \text{ N m}^{-2}$, $T = 328^\circ\text{C}$, $r_0 \approx 0.80 \times 10^2 \text{ N m}^{-2} \text{ min}^{-1}$.

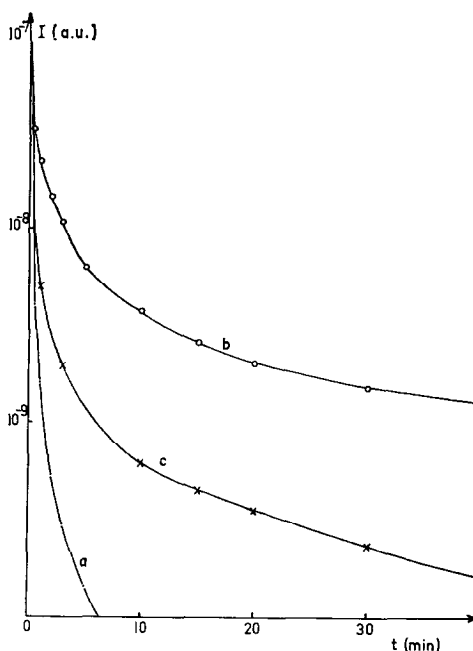


FIG. 3. Semilogarithmic representation of intensity (in arbitrary units) vs time during luminescence on ThO_2 "A." (a) Admission of oxygen alone, $P_0 = 47 \times 10^2 \text{ N m}^{-2}$, $T = 320^\circ\text{C}$; (b) mixture $2 \text{ CO} + \text{O}_2$, $P_0 = 135 \times 10^2 \text{ N m}^{-2}$, $T = 314^\circ\text{C}$; (c) mixture $2 \text{ CO} + 4 \text{ O}_2$, $P_0 = 267 \times 10^2 \text{ N m}^{-2}$, $T = 314^\circ\text{C}$.

ments) and a photon counter (Model 1110 SSR Instruments). An appropriate filter (e.g., M.T.O. Athervex T.2 type) cut off the thermal radiation emitted by the furnace. A grating scanning monochromator Huet M 25 type was interposed in front of the photomultiplier window when the spectrum was to be recorded. All the spectra given below are corrected according to the spectral response of the light analyzing device and to the total intensity decrease as a function of time. The results obtained were quite independent of the different apparatus used.

RESULTS

Thermocouples located in direct contact with the catalyst powder indicated a rise of a few degrees on gas admission. This

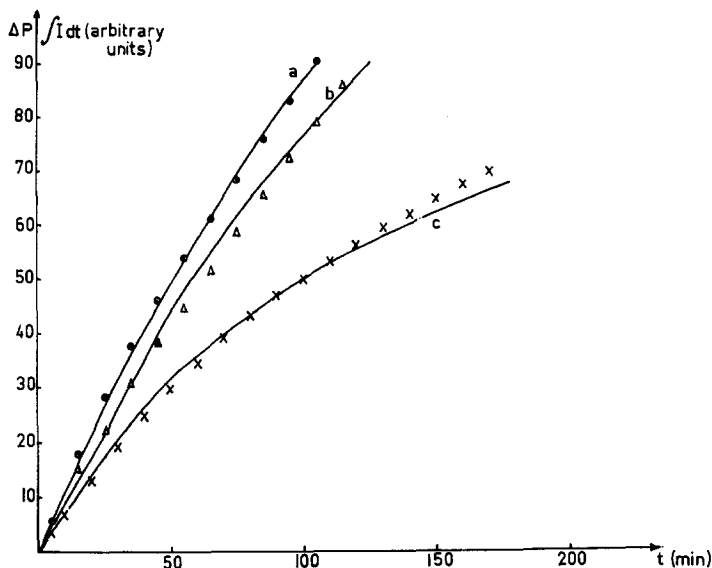


FIG. 4. Luminescence on ThO_2 "A": ΔP and $\int_0^t I dt$ as functions of time. (a) $6 \text{ CO} + \text{O}_2$, $P_0 = 313 \times 10^2 \text{ N m}^{-2}$, $T = 326^\circ\text{C}$; (b) $6 \text{ CO} + \text{O}_2$, $P_0 = 313 \times 10^2 \text{ N m}^{-2}$, $T = 314^\circ\text{C}$; (c) $2 \text{ CO} + \text{O}_2$, $P_0 = 135 \times 10^2 \text{ N m}^{-2}$, $T = 328^\circ\text{C}$.

fact, together with the spectra presented below, excludes the occurrence of an incandescence due to thermal effects.

The results obtained lead us to distinguish between thoria A and thoria B.

1. Thoria A

Figure 2 enables the light intensity curves during oxygen adsorption (curve a) and during catalysis (curves b and c, d) to be compared. It can readily be seen that the

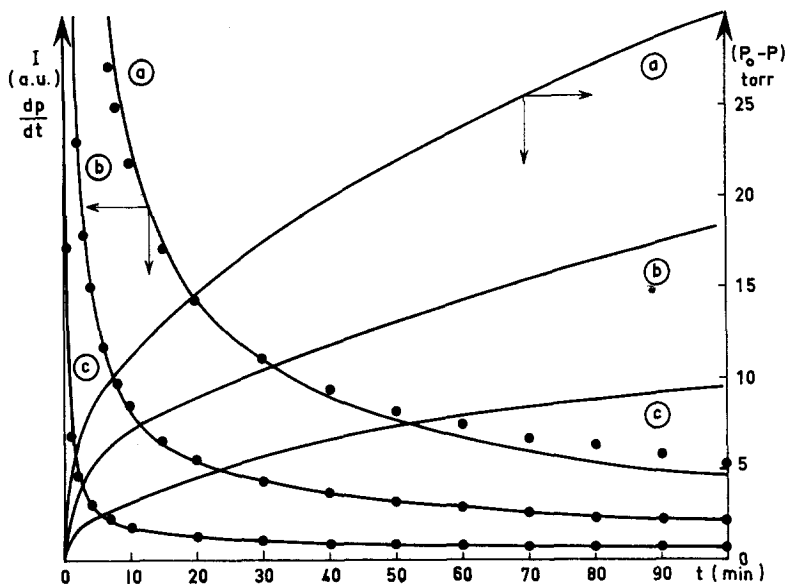


FIG. 5. Luminescence given by the mixture $2 \text{ CO} + \text{O}_2$ on ThO_2 "A." (—) pressure vs time (pressure scale on the right axis) and intensity vs time (intensity scale on the left axis); (●) calculated values of $-(dP/dt)$. (a) $P_0 = 185 \times 10^2 \text{ N m}^{-2}$, $T = 307^\circ\text{C}$; (b) $P_0 = 195 \times 10^2 \text{ N m}^{-2}$, $T = 283^\circ\text{C}$; (c) $P_0 = 183 \times 10^2 \text{ N m}^{-2}$, $T = 255^\circ\text{C}$.

latter curves correspond to a stronger light emission than the former. Moreover, if we provisionally take the initial rate r_0 as a catalytic activity scale and if we ignore the transient phenomena occurring during the first 10 min, we see that curves b and c, d are positioned according to that scale. In particular, the sole curve c, d corresponds to two different mixtures at two different temperatures, but reacting at the same initial rate.

Figure 3 presents the case of the oxygen rich mixture $2 \text{ CO} + 4 \text{ O}_2$, for which the inhibiting role of oxygen has long ago been reported (12). Accordingly, the intensity is lower.

The preceding qualitative assertions can be quantitatively ascertained by a check of relationship (2). This check may con-

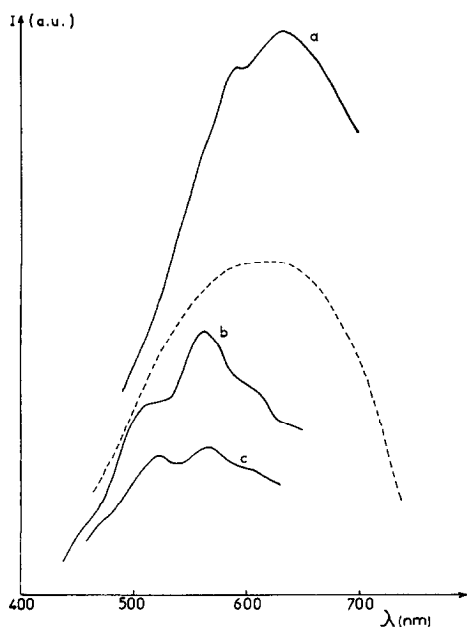


FIG. 6. Spectral distributions during luminescence on ThO_2 "A." (a) $2 \text{ CO} + \text{O}_2$ $P_0 = 188 \times 10^2 \text{ N m}^{-2}$, $T = 292^\circ\text{C}$, after a contact time of 1.5 min; (b) $6 \text{ CO} + \text{O}_2$ $P_0 = 319 \times 10^2 \text{ N m}^{-2}$, $T = 334^\circ\text{C}$, after a contact time of 3 min; (c) same experiment as for (b), after a contact time of 10 min. The broken curve corresponds to the oxygen adsorboluminescence on ThO_2 "A" ($P_0 = 69 \times 10^2 \text{ N m}^{-2}$, $T = 286^\circ\text{C}$). Only curves (b) and (c) correspond to the same ordinate scale.

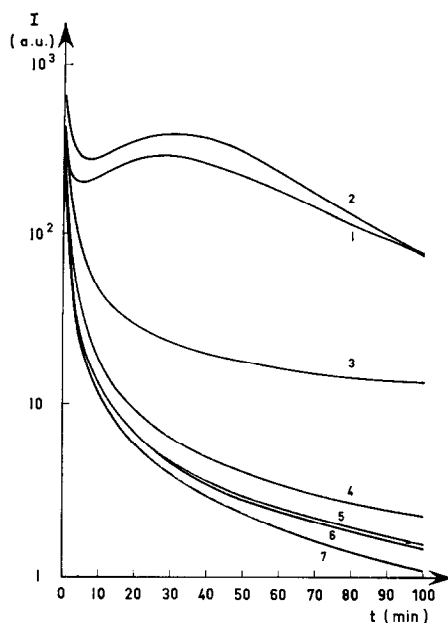


FIG. 7. Luminescence observed with ThO_2 "B." $P_{\text{O}_2} = 65 \times 10^2 \text{ N m}^{-2}$, $T = 287^\circ\text{C}$; (1) oxygen alone; (2) $\text{O}_2 + 0.01 \text{ CO}$; (3) $\text{O}_2 + 0.05 \text{ CO}$; (4) $\text{O}_2 + 0.1 \text{ CO}$; (5) $\text{O}_2 + 0.5 \text{ CO}$; (6) $\text{O}_2 + \text{CO}$; (7) $\text{O}_2 + 2 \text{ CO}$.

sist either in plotting quantities proportional to the pressure variation ΔP and to $\int_{t_0}^t I dt$ as functions of time, as shown by Fig. 4, or in looking at how the dots representing $-(dP/dt)$ are located with respect to the $I(t)$ curves, as shown by Fig. 5. In both cases, the agreement is substantial.

The second characteristic of the light emitted during this catalysis, i.e., its spectral composition, is shown in Fig. 6, where the different curves correspond to different observation periods. Curve a is obtained after a 1.5 min contact time with ThO_2 A at 292°C : it differs from the spectrum recorded during oxygen adsorboluminescence on the same thoria surface (broken curve) only by the shoulder at 580 nm. Curves b and c which have been obtained after longer contact times show an emission band shifted towards shorter wavelengths with peaks at 520, 565 and 610 nm. The relative importance of the last one decreases with time.

2. Thoria B

Figure 7 exhibits in semilogarithmic representation the light intensity change with time when different mixtures $x\text{CO} + \text{O}_2$ are contacted with thoria B. The corresponding curves stand out in sharp contrast to the preceding ones:

a. Only for small values of x ($x \sim 0.01$) is the luminescence greater than with oxygen alone;

b. Luminous intensity decreases when x increases, whereas the catalysis rate is an increasing function of P_{CO} (10).

These two facts eliminate the occurrence of a luminescence due to catalysis proper. This is confirmed by the spectral distribution of the light emitted, shown by Fig. 8. Curve b, obtained with the stoichiometric mixture $2\text{CO} + \text{O}_2$ does not fundamentally differ from curve a, obtained with oxygen alone.

DISCUSSION

Distinguishing between the luminescences due to adsorption and to catalysis, as

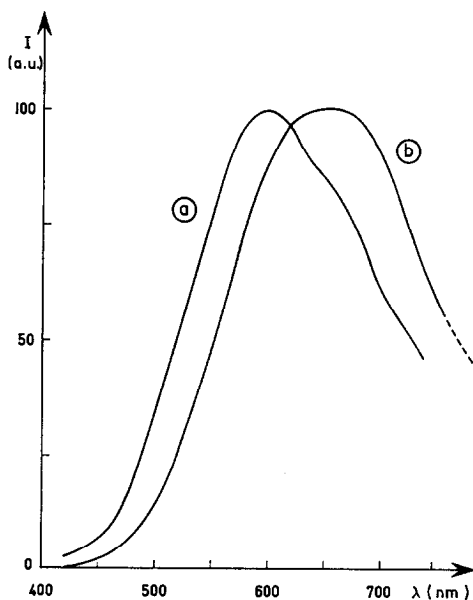
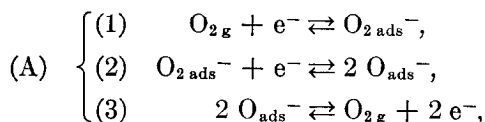


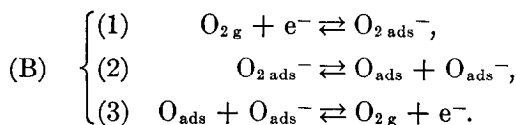
FIG. 8. Luminescence observed with ThO_2 "B." (a) Oxygen alone; (b) mixture $2\text{CO} + \text{O}_2$ $P_0 = 180 \times 10^2 \text{ N m}^{-2}$, $T = 295^\circ\text{C}$.

mentioned in the Introduction, implies looking back at the main characteristics of the former. First of all, adsorboluminescence is observed only when oxygen is contacted with thoria (5). Notably, small amounts of hydrogen (and of CO on thoria B, as shown by Fig. 7) enhance its intensity, owing to a synergy effect (4). The behavior of oxygen species on thoria surfaces, as can be inferred from numerous previous studies (10, 12-14), plays a key role in the interpretation of its ability to react with CO. Formation of the superoxide ion O_2^- by adsorption of gaseous oxygen has been unambiguously demonstrated by ESR experiments (13, 14). Moreover, it is established that O_2^- undergoes a transformation in the adsorbed state, the products of which are likely to be charged and/or neutral oxygen atoms. More precisely, there are at least some hints that the former are more numerous on ThO_2 "A" surfaces than on ThO_2 "B" surfaces (10, 13), so that the sequences of oxygen adsorption on both surfaces can be depicted in the following way:

on thoria "A"



on thoria "B"

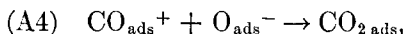


There is also conclusive evidence (10, 12, 15, 16) that the rate determining step in CO oxidation on thoria is the surface reaction between adsorbed CO and adsorbed oxygen atoms.

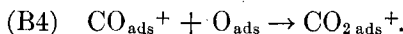
It has recently been shown (17) that the adsorbed CO species is partially in the form of a *slightly* positive adsorbate $\text{CO}^{\delta+}$ ($\delta < 1$). For the sake of simplicity, we shall consider that the reactive form is

CO_{ads}^+ and that the rate determining step can be written:

on thoria A



and on thoria B



It is interesting to note at this stage that the sequence (A1, 2, 3) on thoria "A" allows us to justify the order $-(1/2)$ with respect to oxygen which has been observed at higher pressures of this reactant (12). It is easy to show that

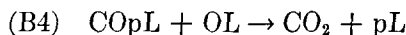
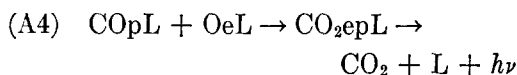
$$(\text{O}_{\text{ads}}^-) = \frac{N(P_{\text{O}_2}/K_3)^{\frac{1}{2}}}{1 + K_1 P_{\text{O}_2} + (P_{\text{O}_2}/K_3)^{\frac{1}{2}}},$$

where N is the initial concentration of available electrons and K_1 and K_3 are equilibrium constants. At large enough oxygen pressures, the second term of the denominator predominates, so that $(\text{O}_{\text{ads}}^-)$ becomes inversely proportional to $(P_{\text{O}_2})^{\frac{1}{2}}$, and the expression when introduced into the rate equation of step (A4) leads to the order $-\frac{1}{2}$ with respect to oxygen.

Another noteworthy point is that the two styles (A4) and (B4) represent only two particular cases, since it is possible to consider other ones for the same rate determining step, as has previously been discussed (13). They simply mean that on the surface of thoria A, the relative abundance of O^- ions makes the reaction (A4) predominate, whereas on thoria B, the reactive oxygen is mostly in the form of O atoms, and the reaction (B4) is favored.

The question is now how these considerations can be related to the present luminescence observations. The most straightforward answer is that reaction (A4) is accompanied by luminescence, whereas reaction (B4) is not. The luminescence observed with thoria B is solely due to oxygen adsorption, i.e., is an adsorboluminescence, more or less influenced by the pressure of CO. In other words, part of the

energy created by (A4) is released in a radiative way, whereas this is not the case for (B4). Moreover, the species responsible for this emission is to be related to the simultaneous presence at the surface of carbon monoxide and oxygen charged species, since the bands at 520 and 565 nm (i.e., about 2.3 eV) are not found in oxygen adsorboluminescence. The electronic theory of catalysis, as described in Refs. (18) and (19), provides the clue to the electronic transition responsible for this chemiluminescence. Rewritten with the symbolism of this theory, reactions (A4) and (B4) take the form:



Here L designates the lattice, pL a hole belonging to the solid, COpL a CO^+ adsorbate, OeL a O^- adsorbate. $\text{CO}_{2\text{epL}}$ is a "weak" (electrically neutral) form of chemisorbed CO_2 . This CO_2 is bound to an exciton which does not preexist, but which is formed during the actual course of the surface reaction, and could be called, for this reason, a "virtual" exciton. CO_2 desorption is thus accompanied by the exciton annihilation, i.e., by the emission of the corresponding quantum. This is no longer the case for the reaction (B4).

In conclusion, a chemiluminescence due to catalysis seems to have been characterized for the first time in the case of CO oxidation on ThO_2 "A." This new technique of investigation of catalysis has the advantages of great sensitivity and of not requiring any external source of irradiation (as in conventional spectroscopy techniques). It appears to be a new tool in the detection and characterization of intermediates taking part in catalysis.

ACKNOWLEDGMENTS

One of us (R.J.J.W.) wishes to express his thanks to the Consejo Nacional de Investigaciones Cientificas y Tecnicas, Argentina, for the scholarship he

was granted during his work on this subject. We are indebted to Miss Sauvan and Mr. Martin for help in the preparation of the manuscript.

REFERENCES

1. Rufov, Y. N., Kadushin, A. A., and Roginskii, S. Z., *Dokl. Akad. Nauk S.S.S.R.*, **171**, 905 (1966).
2. Breysse, M., Faure, L., Claudel, B., and Veron, J., in *Prog. Vac. Microbalance Techn.*, Vol. 2, p. 229. Heyden, London, 1973.
3. Breysse, M., Faure, L., Claudel, B., and Veron, J., *Le Vide* **28**, 72 (1973).
4. Breysse, M., Claudel, B., Faure, L., and La-treille, H., *Faraday Discuss.* **58**, 205 (1974).
5. Breysse, M., Claudel, B., Guenin, M., and Faure, L., *Chem. Phys. Lett.* **30**, 149 (1975).
6. Bressat, R., Breysse, M., Claudel, B., Sautereau, H., and Williams, R. J. J., *J. Luminescence* **10**, 171 (1975).
7. Roginskii, S. Z., and Rufov, Y. N., *Kinet. Katal.* **11**, 383 (1970).
8. Bressat, R., Claudel, B., Puaux, J. P., Williams, R. J. J., Breysse, M., and Faure, L., *J. Catal.*, **40**, 286 (1975).
9. Boudart, M., "Kinetics of Chemical Processes," p. 82. Prentice Hall, Englewood Cliffs, N. J., 1968.
10. Breysse, M., *Ann. Chim.* **2**, 367 (1967).
11. Watson, J. S., *Canad. J. Technol.* **34**, 373 (1956).
12. Veron, J. PhD dissertation, Lyon, 1963; *French A.E.C. Report No. 2392* (1963).
13. Breysse, M., Claudel, B., and Veron, J., *Kinet. Katal.* **14**, 102 (1973).
14. Breysse, M., Claudel, B., and Meriaudeau, P., *J. Chem. Soc. Faraday Trans. 1*, **72**, 1 (1976).
15. Claudel, B., Juillet, F., Trambouze, Y. and Veron, J., *Proc. Int. Congr. Catal.*, 3rd, 1964, p. 214 (1965).
16. Breysse, M., Claudel, B., Prettre, M., and Veron, J., *J. Catal.* **24**, 106 (1972).
17. Meriaudeau, P., Breysse, M., and Claudel, B., *J. Catal.* **35**, 184 (1974).
18. Wolkenstein, T., "The electron Theory of Catalysis on Semiconductors." Pergamon, Elmsford, N. Y., 1963.
19. Wolkenstein, T., *Physico-Chimie de la Surface des Semiconducteurs*, Moscow, 1977.