$\zeta \equiv k_7(\text{NO})_2 - (\epsilon - 1)k_6(\text{NO})$

$\kappa \equiv \theta/[\alpha(\text{RH})_0]$

$\nu \equiv (\text{NO}_2)_0/(\text{NO})_0$

$\rho \equiv Q/\nu$

$\tau \equiv 1/[\alpha(\text{NO}_2)_0(\text{RH})_0]$

*Notation from Friedlander and Seinfeld (1969)*

$\alpha \equiv \gamma k_6 k_4'$

$\beta \equiv k_1/k_3$

$\gamma \equiv k_1/k_2$

$\lambda \equiv \gamma k_7 k_4'$

$\mu \equiv \beta k_5$

$\theta \equiv \gamma k_4$

$\epsilon \equiv$ a branching factor accounting for possible production of more R· than consumed in Reaction 6 below

$k_1 \equiv$ rate constant for $\text{NO}_2 \xrightarrow{h\nu} \text{NO} + \text{O}$, includes light intensity

$k_2 \equiv$ rate constant for $\text{O} + \text{O}_2 \xrightarrow{M} \text{O}_3$, includes third body M and $\text{O}_2$ concentration

$k_3 \equiv$ rate constant for $\text{O}_3 + \text{NO} \rightarrow \text{NO}_2 + \text{O}_2$

$k_4 \equiv$ rate constant for $\text{RH} + \text{O} \rightarrow \text{R·} + \text{Products}$, where RH and R· are generalized hydrocarbon and free radical, respectively

$k_5 \equiv$ rate constant for $\text{RH} + \text{O}_3 \rightarrow$ products (including R·)

$k_6 \equiv$ rate constant for $\text{NO} + \text{R·} \rightarrow \text{NO}_2 + \text{R·}$

$k_7 \equiv$ rate constant for $\text{NO}_2 + \text{R·} \rightarrow$ products (including PAN)

$k_4' \equiv k_4/\zeta$

*Literature Cited*

Abramowitz, M., Stegun, I. A., "Handbook of Mathematical Functions," Applied Mathematics Series 55, National Bureau of Standards, 1964.

Bruijn, N. G. de, "Asymptotic Methods in Analysis," Chap. I, North-Holland Publishing, Amsterdam, Holland, 1961.

Cole, J. D., "Perturbation Methods in Applied Mathematics," Chap. I. Blaisdell, Waltham, MA, 1968.

Erdélyi, A., Ed., "Higher Transcendental Functions," Chap. I, Vol. 1, McGraw-Hill, New York, NY (1953).

Erdélyi, A., "Asymptotic Expansions," Dover, New York, NY (1956).

Friedlander, S. K., Seinfeld, J., ENVIRON. SCI. TECHNOL., 3, 1175 (1969).

Hidy, G., Mueller, P. K., Tokiwa, I., Twiss, S., "Aerometric Factors Affecting the Evolution of the Pasadena Aerosol," J. Colloid Interface Sci., in press, 1972.

Knopp, K., "Theory and Application of Infinite Series," 2nd English ed., p 247, Hafner, New York, NY, 1948.

## COMMUNICATIONS

# Singlet O₂ Production from Photoexcited NO₂

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■ Mixtures of $\text{NO}_2$ and $\text{O}_2$ were irradiated with visible light. ($\lambda > 4000\text{Å}$). Electronically excited $\text{NO}_2$ was produced which transferred energy collisionally to $\text{O}_2$ to produce $\text{O}_2(^1\Delta_g)$. The population of $\text{O}_2(^1\Delta_g)$ in the reaction cell was determined by monitoring its phosphorescent emission at 1.27 $\mu$ with an RCA 7102 photomultiplier used in a photon-counting mode. From the experimentally determined rate of production and destruction of $\text{O}_2(^1\Delta_g)$, the probability that a quenching collision of $\text{NO}_2^*$ with $\text{O}_2$ will produce $\text{O}_2(^1\Delta_g)$ is found to be $\alpha = 0.01 \pm 0.002$. This mechanism is capable of producing a steady-state $\text{O}_2(^1\Delta_g)$ concentration in the atmosphere of $10^7$–$10^8$ cm$^{-3}$.

The possibility that singlet molecular oxygen might play a noticeable role in the photochemical smog cycle was pointed out by Pitts (1969). Herron and Huie (1969) found the relative reactivities of single molecular oxygen, oxygen atom, and ozone to be $10^{-3}:1:1$ at best and concluded that known mechanisms for producing metastable $\text{O}_2$ molecules were not sufficiently effective to make these species important in the smog cycle. Subsequent work indicates the reactivity ratio may be more like $10^{-4}:1:1$ (Johnston et al., 1971). About the same time, Kummler and Bortner (1969), Steer et al. (1969b), and Snelling (1968) showed that benzaldehyde, benzene, naphthalene, and naphthalene derivatives could absorb light and transfer this energy to $\text{O}_2$ to produce excited oxygen molecules. Still, these mechanisms seem too inefficient to be important for smog formation because of the low ambient concentrations of the photosensitizing species and their small extinction coefficients in the visible or near-uv spectral regions.

We have investigated another possible mechanism for generating singlet molecular oxygen, the production of $\text{O}_2(^1\Delta)$ by the $\text{NO}_2$-photosensitized process

$$\text{NO}_2 + h\nu \rightarrow \text{NO}_2^* \tag{1}$$

$$\text{NO}_2^* + \text{O}_2 \rightarrow \text{NO}_2 + \text{O}_2(^1\Delta) \tag{2}$$
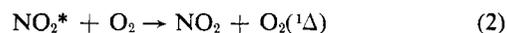
This process was studied by irradiation of $\text{NO}_2$–$\text{O}_2$ mixtures with a chopped, carefully filtered beam of visible light. Wavelengths below 4000Å were excluded to avoid photodissociation of the $\text{NO}_2$ (Douglas and Huber, 1965; Schuck et al., 1966; Cvetanovic, 1964). Direct measurement of the 1.27-$\mu$ emission from the process $\text{O}_2(^1\Delta) \rightarrow \text{O}_2(^3\Sigma) + h\nu$ was used to monitor the energy transfer. Emission was observed through two Corning No. 7-56 filters with an RCA 7102 photomultiplier operated as a photon counter. The emission was confirmed as originating only at 1.27 $\mu$ by scanning the line with a temperature-tuned, narrow band interference filter (Razdow Optical Instruments, 1.2728 $\mu$ peak transmission at 20°C). The photomultiplier tube was calibrated against a blackbody source with various filter combinations. Under our operating conditions, the quantum efficiency of the tube at 1.27 $\mu$ is $1.5 \times 10^{-7}$. The observed signal was about 4 counts/sec. Modulation at 30 Hz was as follows: The sample was irradiated during the first $^1/_4$ cycle; after $^1/_8$-cycle delay, the photomultiplier

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was gated on for $1/2$ cycle, the final $1/8$ cycle was dead time.

The pressure dependence of both the near-ir and visible $NO_2$ emission gave Stern-Volmer plots which yielded values for $NO_2$ quenching by $N_2$ and by $O_2$ in essential agreement with those in the literature (Meyers et al., 1966; Schwartz, 1968).

In a typical experiment, $p(NO_2) \cong 0.48$ torr, $p(O_2) \cong 3.0$ torr, and the system absorbs approximately $5.4 \times 10^{15}$ photons/sec, all in the wavelength range 4000–5000Å. From geometric factors and the observed rate of emission by $O_2(^1\Delta)$, we estimated a total $O_2(^1\Delta)$ production rate of $4.1 \times 10^{13}$/sec. These diffuse uniformly throughout a cell of 860 $cm^3$, in the irradiation interval. Deactivation of excited $O_2$ molecules is due to wall collisions, to collisions with $NO_2$, to collisions with $O_2$ and, in very small part, to radiation. The pseudo first-order rate coefficients for the first three processes are 0.10 $sec^{-1}$ (in our system), 0.08 $sec^{-1}$, and 0.21 $sec^{-1}$, respectively (Becker et al., 1971; Steer et al., 1969a); the radiative rate is $2.58 \times 10^{-4}$ $sec^{-1}$. The system is in a steady state with respect to $O_2(^1\Delta)$, with an effective total first-order decay constant of 0.39 $sec^{-1}$.

From the known quenching constants (Meyers et al., 1966; Schwartz, 1968) for $NO_2*$ by $NO_2$ ($7.1 \times 10^{-11}$ $cm^3$/mol-sec), the measured concentrations of $NO_2$ and $O_2$, and the knowledge that $NO_2$ fluorescence is completely quenched, we determine that fraction of photons absorbed which go one way or another to $O_2$. From the experimentally determined rate of production (and destruction) of $O_2(^1\Delta)$, we thus determine the probability, $\alpha$, that a quenching collision of $NO_2*$ with $O_2$ will produce $O_2(^1\Delta)$:

$$\alpha = 0.01 \pm 0.002 \qquad (3)$$

The uncertainty is due largely to uncertainties in collection efficiency from molecules away from the optic axis of the photomultiplier. In other words, about 1% of the collisions of $NO_2*$ with $O_2$ yield a metastable $O_2(^1\Delta)$.

The possible significance of this observation for the problem of smog appears when we estimate the ambient concentration of $O_2(^1\Delta)$ from the $NO_2$-activated process alone. The rate constant for quenching of $NO_2*$ by $N_2$ is $3.1 \times 10^{-11}$ $cm^3$/mol-sec, slightly less than that for quenching by $O_2$. From these two coefficients, we infer that about 21.5% of the $NO_2*$ in the atmosphere lose their energy to $O_2$, and thus about 0.215% of the excited $NO_2*$ molecules generate $O_2(^1\Delta)$. ($NO_2$ fluorescence is, of course, completely quenched in the atmosphere.) The rate of production of $NO_2*$ by light in the 4000–5000Å region, when the $NO_2$ concentration is 0.035 ppm and the photon flux in the 4000–5000Å interval is $5 \times 10^{16}$/$cm^2$-sec—corresponding to the sun 40° from the zenith, on a clear day—is about $2.3 \times 10^{10}$/$cm^3$-sec. Hence the rate of production of $O_2(^1\Delta)$ under these conditions is about $4.35 \times 10^7$/$cm^3$-sec. The $O_2(^1\Delta)$ is in a steady-state condition, with most of its quenching accomplished by $O_2$; the rate coefficient for this process is $2.2 \times 10^{-18}$ $cm^3$/mol-sec. Hence the pseudo first-order rate coefficient for deactivation of $O_2(^1\Delta)$ is 12 $sec^{-1}$, and the steady-state concentration of $O_2(^1\Delta)$ under the conditions just described is $3.6 \times 10^6$/$cm^3$.

More generally, we can express the steady-state concentration of $O_2(^1\Delta)$, in molecules/$cm^3$, in terms of the photon flux $\phi$ (as $10^{16}$ photons/$cm^2$-sec) and the $NO_2$ concentration (in the common units of ppm) as

$$[O_2(^1\Delta)] = 2 \times 10^7 (NO_2, ppm)\phi \qquad (4)$$

Under conditions of intense sunlight and moderately high concentrations of $NO_2$, the steady-state concentration of

$O_2(^1\Delta)$ easily exceeds $10^7$ $cm^{-3}$ and may reach $10^8$ $cm^{-3}$ as a result of the $NO_2$-activated mechanism alone. The concentration of O atoms is probably seldom greater than $5 \times 10^5$ $cm^{-3}$ (Berry and Lehman, 1971) and may be up to an order of magnitude lower than this during earlier stages of the smog cycle (Johnston et al., 1971). It thus appears the $NO_2$-activated mechanism by itself is capable of producing sufficient $O_2(^1\Delta)$ to make singlet molecular oxygen a contributor to smog formation despite the $10^3$–$10^4$-fold lower activity of the molecular species.

Early work on the photooxidation of hydrocarbons in the presence of $NO_2$ (Bufalini and Altshuller, 1967) indicated that the rate of hydrocarbon oxidation could be explained solely on the basis of O-atom oxidation. However, it should be noted that these experiments were conducted using uv light which photodissociates $NO_2$ to NO + O quite efficiently and produces very little $NO_2*$. Thus these early experiments were under conditions where $[O_2(^1\Delta)] \ll 10^4$ (O) and therefore have no bearing either positive or negative on the role of $O_2(^1\Delta)$ in the atmospheric oxidation of hydrocarbons.

In addition to the high $NO_2$ concentration experiments mentioned above, we have conducted experiments with the $NO_2$ concentration as low as 500 ppm and find the mechanism for $O_2(^1\Delta)$ formation remains operative. This strongly indicates that the energy transfer is truly an elementary molecular process and thus our extension to the atmosphere is valid.

After this work was submitted for publication, we learned that very similar conclusions have been reached by Jones and Bayes (1971) based on a very different detection method.

A more detailed discussion, including a study of the $^1\Sigma$ state, is in preparation.

*Literature Cited*

Becker, K. H., Groth, W., Schuarth, U., *Chem. Phys. Lett.*, **8**, 259–62 (1971).
Berry, R. S., Lehman, P. A., *Annu. Rev. Phys. Chem.*, 47–84 (1971).
Bufalini, J. J., Altshuller, A. P., ENVIRON. SCI. TECHNOL., **1**, 133–8 (1967).
Cvetanovic, R. J., *J. Air Pollut. Contr. Ass.*, **14**, 208–12 (1964).
Douglas, A. E., Huber, K. P., *Can. J. Phys.*, **43**, 74–81 (1965).
Herron, J. T., Huie, R. E., *J. Chem. Phys.*, **51**, 4164–5 (1969).
Johnston, H. S., Pitts, J. N., Lewis, J., Zafonte, L., Mottershead, T., University of California Project Clean Air Task Force Report No. 7, 1971.
Jones, I. T., Bayes, K. D., "Energy Transfer from Electronically Excited $NO_2$," *Chem. Phys. Lett.*, **11**, 163 (1971).
Kummler, R. H., Bortner, M. H., ENVIRON. SCI. TECHNOL., **3**, 944–5 (1969).
Meyers, G. H., Silver, D. M., Kaufman, F., *J. Chem. Phys.*, **44**, 718–23 (1966).
Pitts, J. N., *Advan. Environ. Sci.*, **1**, 289 (1969).
Schuck, E. A., Stephens, E. R., Schrock, R. R., *J. Air Pollut. Contr. Ass.*, **11**, 695–6 (1966).
Schwartz, S. E., PhD thesis, "Kinetics of $NO_2$ Fluorescence," University of California Ernest O. Lawrence Radiation Laboratory, 1968.
Snelling, D. R., *Chem. Phys. Lett.*, **2**, 346–8 (1968).
Steer, R. P., Ackerman, R. A., Pitts, J. N., *J. Chem. Phys.*, **51**, 843–4 (1969a).
Steer, R. P., Sprung, J. L., Pitts, J. N., ENVIRON. SCI. TECHNOL., **3**, 946–7 (1969b).