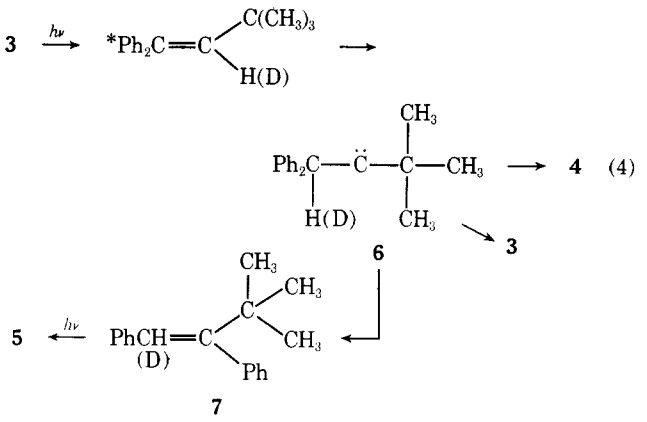

which would be expected from carbene **6**, together with the deuterium-labeling results, provides strong support for the above reaction scheme.

This **3** → **6** transformation, the reverse of which is common in carbene chemistry,[9a] is highly unusual. However, we note that Cristol has very recently found evidence suggesting the migration of a vinyl carbon to form a carbene in the photochemistry of 3-phenylcycloheptene.[11] Likewise, Kropp[12] has provided strong evidence that tetrasubstituted alkenes on direct irradiation form carbenes by a similar vinyl-carbon shift; here, Rydberg excited states are felt to be involved. Both of these processes bear a resemblance to the one we feel is operative in the transformation of **3**, though there are significant differences among all three cases.[13] An interesting aspect of our present case is that there is no evidence for the occurrence of such a carbene formation process in β-*tert*-butylstyrene (**1**), a molecule very similar to **3** which undergoes instead a 1,2-methyl shift to form a cyclopropane (eq 1).[1a,d] This may indicate that the carbene formation from **3** occurs via a twisted excited state ($\pi,\pi^*$), whereas reaction of **1** does not; certainly the congestion about C-1 and the double bond in **3** is more severe than that in the styrene analog **1**, and one would expect twisting to be more favored in the former.[14] Indeed, the reaction looks less unusual if one considers as an intermediate a twisted excited state in which the former olefin $\pi$ electrons occupy nearly perpendicular orbitals. Such an excited state bears some analogy to the n-$\pi^*$ state of ketones and, viewed in this light, the photochemical ring expansion of the n-$\pi^*$ states of cyclic ketones, notably cyclobutanones, to oxacarbenes[15] would then be a reaction very similar to the olefin reaction we report here.

Finally, as mentioned previously, the reaction of **3** appears qualitatively to be very inefficient. This inefficiency is no doubt part of the reason why such carbene formation has not been more generally observed with other olefins, for it would be expected to compete unfavorably with other, more facile processes.

**Acknowledgment.** We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research and Dr. E. Hedaya for a stimulating discussion of the reaction.

### References and Notes

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(3) Irradiations were carried out under $N_2$ with Vycor-filtered light from a Hanovia 450-W mercury arc.
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(8) Irradiation of separately prepared 1,1,2-trimethyl-3,3-diphenylcyclopropane (**8**), the product expected from **3** by analogy with the photochemistry of **1** (eq 1), showed that the **4** and **5** obtained from **3** did not arise via **8**.
(9) W. Kirmse, "Carbene Chemistry", 2nd ed, Academic Press, New York, N.Y., 1971: (a) p 236 ff; (b) pp 457–459.
(10) It is also possible that **7** (and **5**) arises by way of initial phenyl migration in **3*** to form a carbene which then undergoes a β C–H insertion.
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(12) T. R. Fields and P. J. Kropp, *J. Am. Chem. Soc.*, **96**, 7560 (1974).
(13) The reaction observed by Cristol[11] is apparently benzene sensitized, whereas the rearrangements of the tetrasubstituted alkenes do not occur upon sensitization.[12] The transformation of **3** is not a triplet-state process, and a Rydberg excited state would not be involved.
(14) (a) The $^1S$ $\pi,\pi^*$ states of both **1** and **3** would be expected to have minima at twisted geometries. However, the activation energy for reaching this minimum from the planar $^1S$ state is most likely greater for **1** than **3**. A similar steric effect on ease of twisting in $^1S$ is found on comparison of *trans*-stilbene, *cis*-stilbene, and the α-methylstilbenes. See J. Saltiel et al., *Org. Photochem.*, **3**, 1 (1974). See also M. G. Rockley and K. Salisbury, *J. Chem. Soc., Perkin Trans. 2*, 1582 (1973), for a discussion of the potential-energy surface of the $^1S$ and $^2S$ $\pi,\pi^*$ states of β-methylstyrene. (b) An alternative rationale for the difference between **1** and **3** is that both react from twisted $\pi,\pi^*$ states, but that these states differ somewhat in their degree of twisting (e.g., a more nearly 90° twisted geometry in **3** which might be expected to enhance hydrogen migration) and as a consequence show different migratory behavior.
(15) Reference 9, p 47 ff.

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## Structure of Everninomicin D[1]

*Sir:*

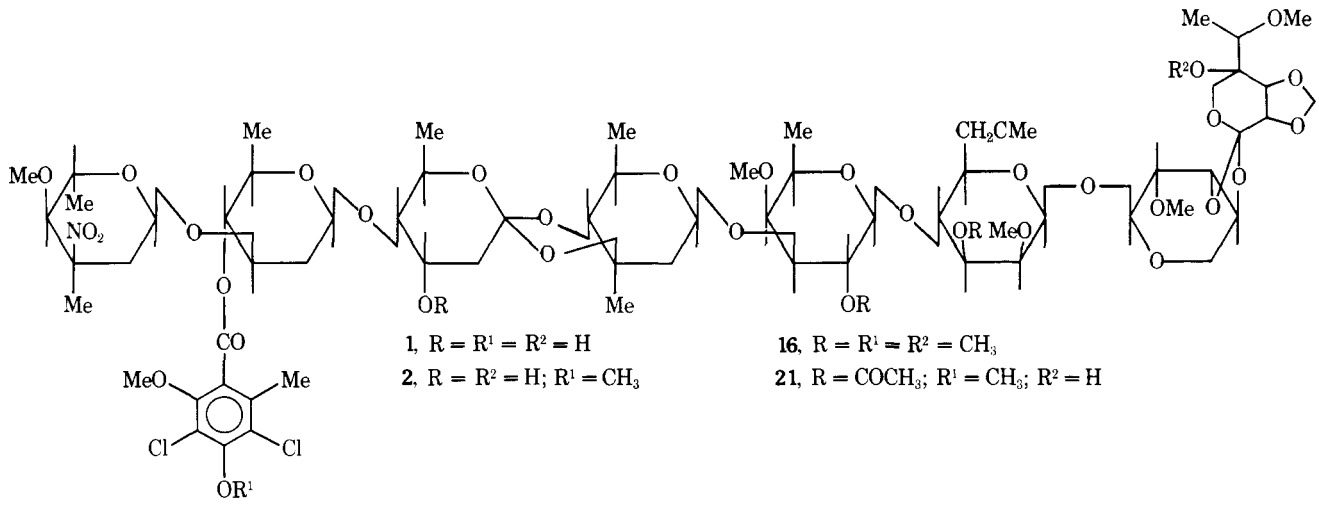
Everninomicins, produced by *Micromonospora carbonaceae*,[2] are oligosaccharide antibiotics, related to curamycin[3a] and avilamycin,[3b] and display high activity against gram positive bacteria and Neisseria including strains resistant to penicillin, tetracycline, lincomycin, rifampicin, macrolides, and chloramphenicol.[4] We report here the structure of the major component, everninomicin D.

Everninomicin D (**1**) is an amorphous solid $C_{66}H_{99}O_{35}NCl_2$: $[\alpha]D = -34.2°$; ir $\nu_{max}$ 1538 (nitro), 1730 $cm^{-1}$ (carbonyl), the nitro absorption was stronger than the carbonyl absorption. It formed a monomethyl ether (**2**) with diazomethane, $C_{67}H_{101}O_{35}NCl_2$: $[\alpha]D = -29.7°$. The molecular weight of **2** was determined to be 1579 (calcd for $C_{67}H_{101}O_{35}NCl_2$ is 1551) by the application of the radioactive method described by us earlier.[5]

Everninomicin D on mild acidic hydrolysis yielded everninomicin $D_1$ (**3**), $C_{66}H_{101}O_{36}NCl_2$: $[\alpha]D = -41.2°$; ir $\nu_{max}$ 1538 (nitro), 1730 $cm^{-1}$ (carbonyl). As in everheptose (**4**),[11] compound **3** showed stronger carbonyl absorption than nitro absorption in the ir. On treatment with diazomethane it underwent smooth cleavage to **5** and olgose (**6**).

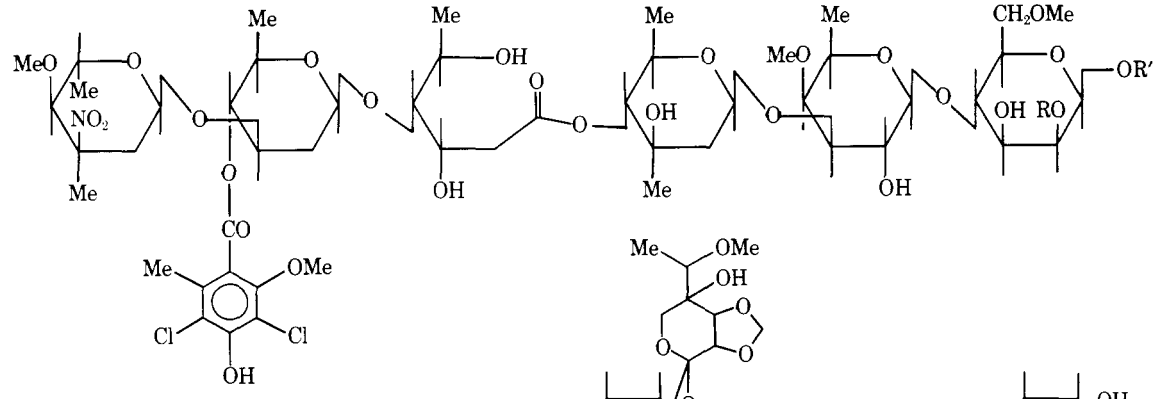
Olgose (**6**) ($C_{37}H_{62}O_{22}$; mp 212–215°; $[\alpha]D = -21.8°$) does not show any carbonyl absorption in the ir. The NMR spectrum of **6** (220 MHz; $CDCl_3$) shows three methyl doublets at δ 1.24, 1.31, and 1.33 ($J$ = 7 Hz), a methyl singlet at δ 1.28, and five methoxyl groups. On solvolysis[6] compound **6** yielded evertetrose[7] (**7**) and an ester, **8**.

Compound **8** distills at 60° (0.4 mm): $C_{10}H_{18}O_7$ ($M^+$ 250); $[\alpha]D = -28°$; ir, $\nu_{max}$ 1739 (ester) and 3509 $cm^{-1}$ (hydroxyl); NMR, δ 1.25 (d, $J$ = 6.5 Hz, $CH_3CH(OMe)$),



1, R = R¹ = R² = H
2, R = R² = H; R¹ = CH₃

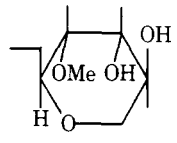
16, R = R¹ = R² = CH₃
21, R = COCH₃; R¹ = CH₃; R² = H

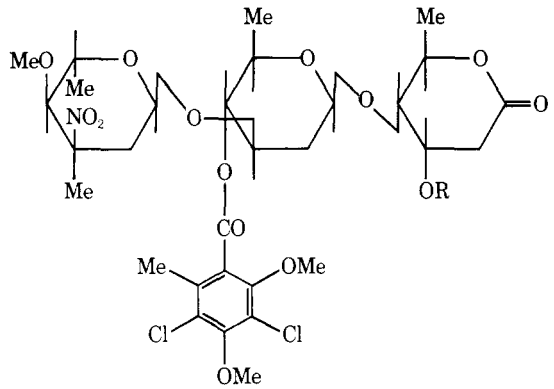


3, R = CH₃; R′ =

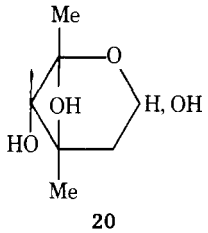


4, R = CH₃; R′ =





5, R = H
17, R = CH₃



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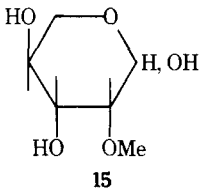
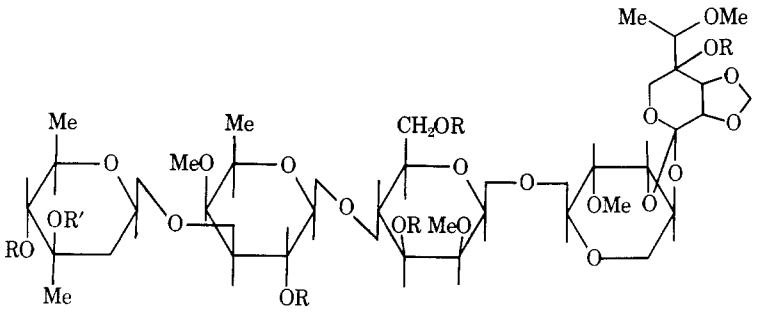


15

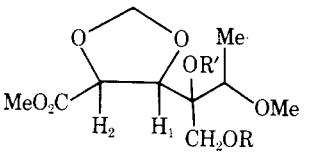
3.35 (s, 3 H, -OMe), 3.81 (s, 3 H, -COOMe), 3.6-3.9 (multiplet; 3 H), 4.19 (d, 1 H, 5 Hz, $H_1$), 4.85 (d, 1 H, $J$ = 5 Hz, $H_2$), 5.0 and 5.21 (s, 1 H each, -O- $CH_2$-O).[8] Compound **8** yielded a monoacetate, **9:** colorless oil; ir $\nu_{max}$ 3546, 1739 $cm^{-1}$; NMR, $\delta$ 4.1, 4.3 (doublets, $J$ = 12 Hz, $-CH_2OAc$). Sodium metaperiodate oxidized **8** to the ketone **10:** colorless oil; $C_9H_{14}O_6$; ir, $\nu_{max}$ 1750 $cm^{-1}$; NMR, $\delta$ 4.95 (d, 1 H, $J$ = 4.5 Hz, $H_2$), 4.71 (d, 1 H, $J$ = 4.5 H, $H_1$), 3.75 (q; $J$ = 6.5 Hz). On heating with aqueous sulfuric acid, compound **10** yielded formaldehyde.

The linkage of **8** to evertetrose (**7**) to reconstitute olgose (**6**) was shown in the following way. Permethylated olgose (**11**) ($C_{42}H_{72}O_{22}$ ($M^+$ 928); mp 194-195°; $[\alpha]_D$ = -13.9°) does not show the presence of any hydroxyl or ester function in the ir. Compound **11** on solvolysis yielded **12** and **13.**

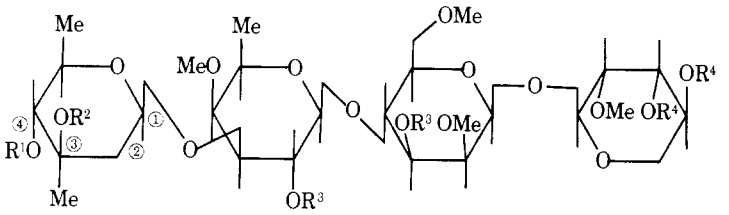
Compound **12** distills at room temperature (0.5 mm): $C_{11}H_{20}O_7$; ir, $\nu_{max}$ 3448 and 1754 $cm^{-1}$. On acetylation compound **12** yielded **14:** colorless liquid; $C_{13}H_{22}O_8$; ir, $\nu_{max}$ 1750 $cm^{-1}$ and no absorption for a hydroxyl group. In the NMR spectrum besides showing the characteristic features for **12** it showed the presence of a $-CH_2OCOCH_3$ group.[9]



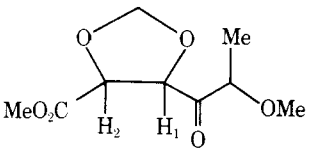
6, R = R′ = H
11, R = R′ = $CH_3$



8, R = R′ = H
9, R = $COCH_3$; R′ = H
12, R = H; R′ = $CH_3$
14, R = $COCH_3$; R′ = $CH_3$



7, $R^1 = R^2 = R^3 = R^4 = H$
13, $R^1 = R^2 = R^3 = CH_3$; $R^4 = H$
18, $R^1 = R^2 = R^4 = H$; $R^3 = CH_3$
19, $R^1 = R^4 = COCH_3$; $R^2 = H$; $R^3 = CH_3$



10

Compound **13** ($C_{32}H_{58}O_{17}$; mp 108–110°; $[\alpha]D$ = −45.1°) does not show carbonyl absorption in the ir. The position of the free hydroxyl groups in **13** was indicated by measuring the CD of the cuprammonium complex[10] of **13**, $[\theta]_{288}$ (−1250) (suggesting k chelate). The formation of a k chelate is possible only if the hydroxyl groups of 2-*O*-methyl lyxose moiety in **13** are free. Compound **11** on prolonged acidic hydrolysis yielded a mixture of products from which 2-*O*-methyl-L-lyxose[10] (**15**) was isolated confirming the above conclusion.

As compound **11** had no carbonyl absorption in the ir and on hydrolysis yielded **12** and **13**, it is evident that the primary hydroxyl group and the ester function of **12** and the hydroxyl groups in **13** must be involved in the linkage of **12** to **13** in the structure of permethylated olgose **11.** To explain the aforementioned observations we propose structure **6** for olgose and **11** for its permethylated derivative. The formation of the hydrolysis products of olgose (**6**) is then explained readily by the opening of the ortho ester function with methanolic *p*-toluenesulfonic acid. The $^{13}C$ NMR spectrum of **6** showed a signal at $\delta$ 119.8 confirming the presence of an ortho ester carbon in olgose (**6**).

Everninomicin $D_1$ (**3**) on hydrolysis yields everheptose[11] (**4**). As **3** and **4** behave similarly in chemical reactions and particularly in their reactions with diazomethane, it follows, therefore, that everninomicin $D_1$ must be represented by the structure **3.**

Everninomicin D (**1**) on exhaustive methylation yielded permethylated everninomicin D[12] (**16**): $C_{72}H_{113}O_{36}NCl_2$; $[\alpha]D$ = −27.8°. On solvolysis **16** yielded a mixture of products, from which the following compounds were isolated: compound **17** ($C_{31}H_{43}O_{14}NCl_2$; mp 129°; $[\alpha]D$ = −46.1° (The NMR and mass spectra of **17** were consistent with the assigned structure. Isolation of **17** from the hydrolysis of **16** indicated that the hydroxyl group $\beta$ to the ester carbonyl in everninomicin $D_1$ (**3**) is free in everninomicin D.); compound **18,** ($C_{30}H_{54}O_{17}$; $[\alpha]D$ = −55°) yielded an amorphous tri-*O*-acetyl derivative **19** which showed besides the other expected features of the molecule a doublet at $\delta$ 4.6 ($J$ = 10 Hz) for $H_4$ proton. As has been pointed out earlier, the two hydroxyl groups in the 2-*O*-methyl lyxose portion of the molecule are linked with **8** in olgose. Therefore, it follows that the two free hydroxyl groups in the evermicose[13] portion of **18** must be involved in the linkage in the structure of everninomicin D (**1**). This is further confirmed by the isolation of **20** from the hydrolysis of compound **16.**

The NMR spectrum of everninomicin D (**1**) showed the presence of 7-methoxyl groups, nine C-methyl groups, and no more anomeric protons than are already accounted for in the structure of everninomicin $D_1$ (**3**). The monomethyl ether of everninomicin D (**2**) yielded a triacetate, **21,** $[\alpha]D$ = −28.1°, as evidenced by the NMR spectrum. Everninomicin D on solvolysis did not yield any products other than those recognized from the hydrolysis of everninomicin $D_1$ (**3**) (followed by TLC, VPC, etc.). We therefore conclude that the conversion of everninomicin D (**1**) to everninomicin $D_1$ (**3**) simply involves the hydrolytic opening of an ortho ester linkage without loss of any component of the molecule.

Based on all the observations presented here we propose structure (**1**) for everninomicin D. The hydrolytic opening of one of the ortho ester linkages in everninomicin D (**1**) yields everninomicin $D_1$ (**3**) and the hydrolysis of both the ortho ester linkages yields everheptose[11] (**4**). The $^{13}C$ NMR spectrum of everninomicin D shows signals at $\delta$ 119.6 and 120.0 confirming the presence of two ortho ester carbons in structure[14] **1.**

Everninomicin D thus represents the first example of a structure elucidation in this group of complex oligosaccharide antibiotics.

## References and Notes


(1) Presented at the (a) Annual Congress of The Chemical Society, England, held at Imperial College, London, in April 1974, and (b) 14th National Medicinal Chemistry Symposium held at the University of New Hampshire in June 1974.
(2) G. H. Wagman, G. M. Luedemann, and M. J. Weinstein, *Antimicrob. Agents Chemother.*, 33 (1964).
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(4) Unpublished work, Dr. J. A. Waitz, Schering Corporation, Bloomfield, N.J.
(5) H. P. Faro, A. K. Ganguly, and D. H. R. Barton, *Chem. Commun.*, 823 (1971).
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(7) A. K. Ganguly, O. Z. Sarre, and S. Szmulewicz, *Chem. Commun.*, 746 (1971).
(8) P. Yates and R. S. Dewey, *Tetrahedron Lett.*, 847 (1962); R. C. Cookson and T. A. Crabb, *Tetrahedron*, **24**, 2385 (1968).
(9) Mass spectral fragmentation of **8**, **9**, **10**, **12**, and **14** were consistent with the assigned structures.
(10) A. K. Ganguly, O. Z. Sarre, and J. Morton, *Chem. Commun.*, 1488 (1969).
(11) A. K. Ganguly, O. Z. Sarre, D. Greeves, and J. Morton, *J. Am. Chem. Soc.*, **95**, 942 (1973).
(12) Under similar conditions olgose (**6**) was converted to permethylated olgose (**11**) wherein all the hydroxyl groups were methylated.
(13) A. K. Ganguly and O. Z. Sarre, *Chem. Commun.*, 1149 (1969).
(14) Satisfactory elementary analyses were obtained for all new compounds; ir spectra were recorded in chloroform solution; optical rotations were measured in chloroform solution; NMR spectra were taken at 100 MHz in $CDCl_3$ with internal TMS standard. All the coupling constant values were obtained using spin–spin decoupling experiments.

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## Facile Spin-Forbidden Reactions. $Ba + SO_2 \rightarrow BaO + SO$

*Sir:*

Violation of the electron spin conservation rule[1] during a collision is rare but not unknown. Among the few fast spin-forbidden processes in the gas phase are the ion–molecule reaction[2] $O^+ (^4S) + CO_2 (^1\Sigma^+) \rightarrow O_2^+ (^2\Pi) + CO (^1\Sigma^+)$ and the quenching[3] of O ($^1$D) by Xe or $N_2$. In condensed media, several examples of singlet to triplet conversion are reported in photochemical studies of organic molecules, for example, the fragmentation of tetramethyl-1,2-dioxetane and the isomerization of napthvalene.[4]

We have used laser-induced fluorescence to examine a spin-forbidden, gas-phase, neutral–neutral reaction

$$Ba(^1S) + SO_2(^1A) \longrightarrow$$
$$BaO(^1\Sigma^+) + SO(^3\Sigma^-) \quad \Delta H = -4.1 \pm 1.3 \text{ kcal/mol}^{5,6} \quad (1)$$

Insufficient energy is available for the spin-allowed production of excited SO(a $^1\Delta$) ($\Delta H$ = 13 kcal/mol).[7] The rate of eq 1 is large,[8] by our measurements four times that of the spin-allowed reaction

$$Ba(^1S) + CO_2(^1\Sigma^+) \longrightarrow$$
$$BaO(^1\Sigma^+) + CO(^1\Sigma^+) \quad \Delta H = -7.8 \pm 1.4 \text{ kcal/mol}^{5,6} \quad (2)$$

despite comparable exothermicities. This observation may be explained by an electron jump mechanism.

The basic apparatus[6,9] is shown schematically in Figure 1. A beam of Ba formed at 860° in the oven chamber reacts with thermal $SO_2$ gas ($10^{-4}$ Torr) in the scattering chamber, under single-collision conditions. A pulsed, tunable dye laser beam, intersecting the Ba beam at right angles, excites a particular vibrational–rotational level of the BaO product. The population of this level can be determined from the intensity of the fluorescence, detected by a photomultiplier mounted beneath the Ba beam–laser beam intersection. We use the dye CSA-22[10] to excite the (5,0), (6,0), (7,1), and (7,2) bands of the BaO ($A\ ^1\Sigma^+$–$X\ ^1\Sigma^+$) system.[11]

Figure 2a shows data from part of a scan of the (5,0) band, from which the rotational populations of BaO ($v$ = 0) in Figure 2b are derived. The vibrational populations are

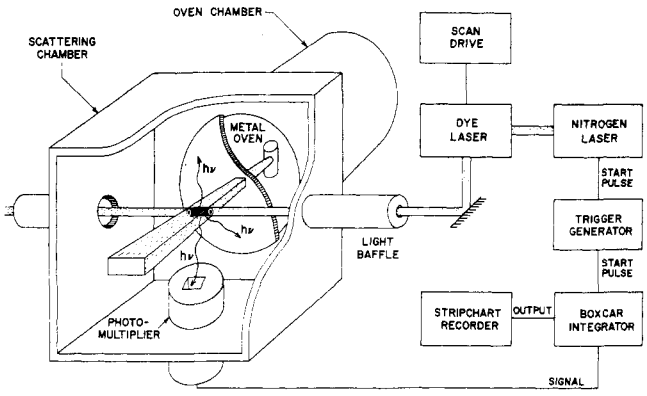


**Figure 1.** Schematic of the laser-induced fluorescence apparatus.

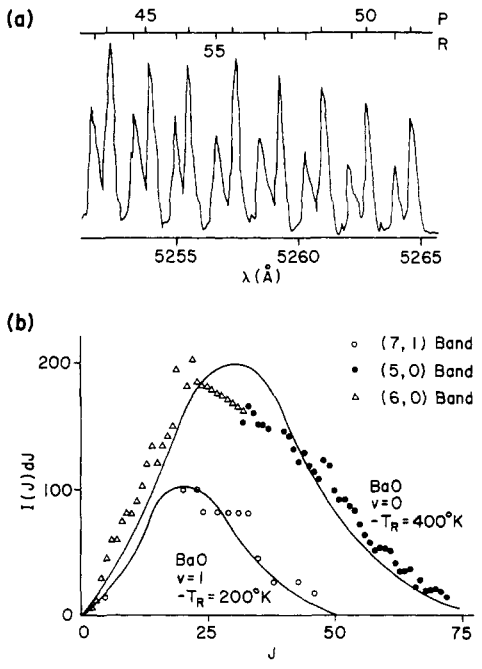


**Figure 2.** (a) A portion of the laser-induced fluorescence spectrum of BaO ($v$ = 0), from a scan of the BaO (A–X) (5, 0) band. The individual rotational lines are labeled. (b) Rotational populations of the BaO product, with the best fitting Boltzmann distributions. The $v$ = 1 values are properly scaled to those for $v$ = 0. The intensity scale is arbitrary.

$v_0$:$v_1$:$v_2$ = 76:24:<4 (no $v$ = 2 was observed). Of the initial relative kinetic energy (~1.1 kcal/mol) and reaction exothermicity, 4.6 ± 1.6 kcal/mol of the energy, on the average, remains for product translation and SO vibrational or rotational energy. This markedly asymmetric distribution of energy indicates a direct reaction mechanism, in agreement with the highly forward peaked angular distribution of BaO reported previously.[8]

Figure 3 shows cuts of relevant Ba–$SO_2$ surfaces and suggests a possible reaction mechanism. The reaction begins with the familiar electron-jump or harpoon mechanism.[12] The crossing of the ionic and neutral surfaces occurs at ~3.5 Å.[13] The ion pair of the doublet species $Ba^+$ and $SO_2^-$ correlates with singlet and triplet states of Ba–$SO_2$, which are split in energy by an exchange integral. At large distances, this integral is small and the two states of the diradical are nearly degenerate. Thus transitions to the triplet surface may be accomplished by spin–orbit[14] or spin–rotation coupling, following the electron jump. This coupling may be appreciable at large distances where the states are nearly degenerate, for in first-order perturbation theory