

ether. The pTpTpTOAc was isolated in 31% yield based on pTpTOAc.

Data on the chromatographic and spectral properties of the compounds which have been prepared are summarized in Table I. The yields of the compounds were determined spectrophotometrically.

Table I. Chromatographic and Spectral Properties of the Reported Compounds

Compd	—Pc ^a solvent—		Spectral data (in H ₂ O, pH = 9)	
	A	B	λ_{\max} (10 ⁻³ e)	λ_{\min}
pT	0.20	0.22		
NpT	0.58		251 (17.2)	230
pTOAc	0.22	0.33		
NpTpTOAc	0.45		255 (25.0)	235
pTpTOAc	0.12	0.29		
pTpT ^b	0.09	0.19		
NpTpTpTOAc	0.24		266 (33.0)	236
pTpTpTOAc	0.05	0.12		
pTpTpT ^b	0.04	0.10		

^a Pc = paper chromatography. Paper chromatography was carried out by the descending technique using Toyo-Roshi no. 51 paper. Solvent systems used were: solvent A, isopropyl alcohol-concentrated ammonium hydroxide-water (7:1:2, v/v); solvent B, ethanol-0.5 M ammonium acetate, pH 3.8 (7:3, v/v). ^b The compound has been reported by Khorana and coworkers (P. T. Gilham and H. G. Khorana, *J. Amer. Chem. Soc.*, **80**, 6212 (1958); H. G. Khorana and J. P. Vizsolyi, *ibid.*, **83**, 675 (1961)). The R_f values of the compounds agree well with those given in the literature and the oligothymidylates prepared by the present method were characterized by degradation to pT with snake venom phosphodiesterase.

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A Comparison of the Reactivities of the Lowest Excited States of Nitrogen ($A^3\Sigma_u^+$) and of Carbon Monoxide ($a^3\Pi$)

Sir:

The long-lived lowest triplet states of nitrogen and carbon monoxide can be produced by discharge-flow techniques in an environment which is suitable for identification of their reactions and the measurement of rate constants.^{1,2} Although both states have nearly the same amount of electronic energy, *i.e.*, $CO(a^3\Pi; v' = 0) = 48,474 \text{ cm}^{-1}$ and $N_2(A^3\Sigma_u^+; v' = 0) = 49,757 \text{ cm}^{-1}$, the CO state arises by excitation of an electron from the 5σ nonbonding to the 2π antibonding orbital, whereas the nitrogen state is formed by promotion of an electron from $1\pi_u$ bonding to the $2\pi_g$ antibonding orbital.³ Both states acquire their metastable nature⁴ from the prohibition of spin change with

(1) (a) D. W. Setser, D. H. Stedman, and J. A. Coxon, *J. Chem. Phys.*, **53**, 1004 (1970); (b) J. A. Meyer, D. W. Setser, and D. H. Stedman, *J. Phys. Chem.*, **74**, 2238 (1970); (c) J. A. Meyer, D. W. Setser, and D. Klosterboer, *J. Chem. Phys.*, in press.

(2) G. W. Taylor and D. W. Setser, *Chem. Phys. Lett.*, **8**, 51 (1971).

(3) G. Herzberg, "Spectra of Diatomic Molecules," Van Nostrand, Princeton, N. J., 1950.

(4) (a) The radiative lifetime of the $N_2(A^3\Sigma_u^+)$ state is 1.3 and 2.6 sec for the $\Sigma = 0$ and ± 1 substates, respectively. D. W. Shamansky and N. P. Carleton, *J. Chem. Phys.*, **51**, 682 (1969). (b) The radiative lifetime of $CO(a)$ is not firmly established, but a value of 7.5 msec recently has been reported: G. M. Lawrence, *Chem. Phys. Lett.*, **9**, 575 (1971);

radiative decay. We wish to report on some interesting differences between the rates of quenching of these two excited states by several simple substrate molecules.

The excited states of N_2 and CO were generated by the interaction of ground-state N_2 and CO_2 , respectively, with metastable $Ar(^3P_{0,2})$ atoms (11.7 eV) in a discharge-flow apparatus; the technique has been described previously for both cases.^{1,2} In the present application, the reaction vessel was a 28-mm i.d. Pyrex tube with three quartz observation windows. The interaction between the CO_2 or N_2 and the metastable argon atoms takes place at the entrance of the flow reactor, and the $CO(a^3\Pi)$ or $N_2(A^3\Sigma_u^+)$ molecules are carried downstream from the interaction zone by the argon carrier gas. The flow velocity was $\sim 2 \times 10^3 \text{ cm sec}^{-1}$ at a flow tube pressure of 1.5–4.0 Torr. Reagents, diluted with 10 parts of pure argon and stored in 5-l. reservoirs, were added either 4.0 or 11.0 cm upstream of the last observation window. Observations were made through the quartz windows perpendicular to the gas flow with a 0.3-m McPherson scanning monochromator equipped with a HTV R212 photomultiplier tube and PAR phase lock detector. The $CO(a^3\Pi)$ concentration was monitored by observing the Cameron bands, $CO(a^3\Pi \rightarrow X^1\Sigma^+)$. In the present study the $N_2(A^3\Sigma_u^+)$ concentration was followed by direct observation of Vegard-Kaplan bands, $N_2(A^3\Sigma_u^+ \rightarrow X^1\Sigma_g^+)$. In our earlier work, the 2537-Å emission from $Hg(^3P_1)$, which is directly proportional to $[N_2(A)]$,^{1b,c,5} was employed to follow the $N_2(A)$ concentration.

The quenching rate constants were measured by using the fixed-observation-point technique in which $[N_2(A)]$ or $[CO(a)]$ was monitored at a fixed distance downstream from the mixing point; we used the last window, 11 cm away from the uppermost addition jet through which quenching gases were added. First-order quenching plots, which followed $I = I_0 \exp(-k_Q \cdot [Q]\Delta t)$, were observed and the slopes of the lines shown in Figure 1 were used to obtain the quenching rate constant, k_Q . The method was checked by adding reagent at a jet 4.0 cm from the observation point, and good agreement was found for the rate constants of all quenching gases.

A summary of the rate constants for both metastables obtained at room temperature is shown in Table I. The rate constants for quenching of $N_2(A)$ determined in this study were somewhat lower than those previously reported from this laboratory. A problem with incomplete mixing was determined to be the cause for this discrepancy. The rate constants measured in this work should be considered lower limits; however, they are probably good to within 50% of the actual values. Except for special cases mentioned in the footnotes of the table, the agreement between the $N_2(A)$ rate constants measured here and the values in the literature is within experimental error.^{1c,6,7} In any event, the relative quenching rate constants of $CO(a)$ and $N_2(A)$ measured in the present apparatus are not affected and may be considered accurate.

R. J. Donovan and D. Hussain, *Trans. Faraday Soc.*, **63**, 2879 (1967), reported a value of 12 msec.

(5) R. A. Young and G. A. St. John, *J. Chem. Phys.*, **48**, 2572 (1968).

(6) R. A. Young, G. Black, and T. G. Slinger, *ibid.*, **50**, 303 (1969).

(7) A. B. Callear and P. M. Wood, *Trans. Faraday Soc.*, **67**, 272 (1971).

Table I. Quenching Rate Constants for $N_2(A^3\Sigma_u^+)$ and $CO(a^3\Pi)$

Quenching molecule	Rate Constant, $\text{cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$	
	$N_2(A^3\Sigma_u^+; v' = 0, 1)^a$	$CO(a^3\Pi; v' = 0)^b$
O_2	$(6.5) \times 10^{-12}$	$1.1 (1.1) \times 10^{-10}$
NO	$(1.1) \times 10^{-10 c}$	1.8×10^{-10}
CO_2	$< 1 \times 10^{-14}$	1.4×10^{-11}
N_2O	1.0×10^{-11}	1.5×10^{-10}
C_2N_2	3.4×10^{-11}	1.9×10^{-10}
CO	$2.5 \times 10^{-11 d}$	$1.4 (1.2) \times 10^{-10}$
N_2		$1.0 \times 10^{-11 e}$
H_2	$< 1 \times 10^{-14}$	$1.4 (1.4) \times 10^{-10}$
D_2	$< 1 \times 10^{-14}$	1.0×10^{-10}
CH_4	$< 1 \times 10^{-14}$	2.4×10^{-10}
C_2H_6	$< 1 \times 10^{-14 h}$	2.8×10^{-10}
C_2H_4	1.4×10^{-10}	3.9×10^{-10}
NH_3	$0.8 \times 10^{-10 f, g}$	$1.8 \times 10^{-10 p}$
SO_2	2.8×10^{-11}	1.1×10^{-10}

^a The rate constants enclosed in parentheses were taken from ref 1c. The $N_2(A)$ rate constants measured in the present apparatus tended to be lower than previous measurements. The difference varied from a few per cent for C_2H_4 and N_2O up to a factor of 2 for ammonia. Measurements in this table should be regarded as lower limits to the true rate constants. ^b Rate constants were measured at a total pressure of either 1.7 or 3.2 Torr. The latter are enclosed in parentheses. ^c W. G. Clark and J. A. Meyer, Kansas State University, unpublished data. ^d This is for the $N_2(A; v' = 1)$ level. Since the reaction between $N_2(A)$ and $CO(X)$ gives $CO(a)$ and $N_2(X)$, and since the reaction is reversible, measurement of this rate constant in excess nitrogen presents some problems and merits further work. ^e At least part of quenching takes place with formation of $N_2(A)$. ^f Our measurement^{1c} is in agreement with ref 6 rather than with ref 7. ^g Both $N_2(A)$ and $CO(a)$ quenching data for NH_3 in this study showed anomalous effects associated with interaction of NH_3 with the wall. These effects were minimized by seasoning the flow tube with a flow of ammonia for several minutes. ^h In contrast to ref 7, no evidence was found for quenching of $N_2(A)$ by C_2H_6 . Care must be exercised to remove impurities, such as C_2H_4 , from the ethane.

The general conclusion to be drawn from the data in Table I is that $CO(a^3\Pi)$ is *much* more reactive than $N_2(A^3\Sigma_u^+)$. This is especially true for CO_2 , H_2 , O_2 , and saturated hydrocarbons. The only reagents that we have found which do not readily quench $CO(a^3\Pi)$ are the perfluoroalkanes. The rate constant for C_2F_6 is $\sim 1.8 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$. The perfluoroalkanes quench $N_2(A)$ even more slowly. Previously, we had established that fast quenching of $N_2(A)$ usually proceeds by transfer of energy to a triplet state of the quenching molecule.^{1b, 8} This also appears to be the case for many of the $CO(a^3\Pi)$ reactions.^{2, 9} The question to be answered is: why do these virtually isoenergetic molecules differ so significantly in their quenching reactions? Inspection of the potential energy curves^{10, 11} of N_2 and CO shows that the internuclear separation in $CO(a^3\Pi)$ is only slightly greater than in the $CO(X)$ state. By contrast, the $N_2(A)$ state is displaced to a much larger internuclear distance than the $N_2(X)$ state. Thus quenching *via* vertical transition processes will release different quantities of energy; *i.e.*, $\sim 4 \text{ eV}$ for $N_2(A)$ and 6.1 eV for $CO(a)$. Quenching by H_2 , *via* the formation of the repulsive triplet

(8) D. H. Stedman, J. A. Meyer, and D. W. Setser, *J. Amer. Chem. Soc.*, **90**, 6856 (1968).

(9) W. G. Clark, Kansas State University, unpublished results.

(10) P. H. Krupenie, "Band Spectrum of Carbon Monoxide," NSRDS-NBS 5, U. S. Government Printing Office, Washington, D. C., 1966.

(11) F. R. Gilmore, *J. Quant. Spectrosc. Radiat. Transfer*, **5**, 369 (1965).

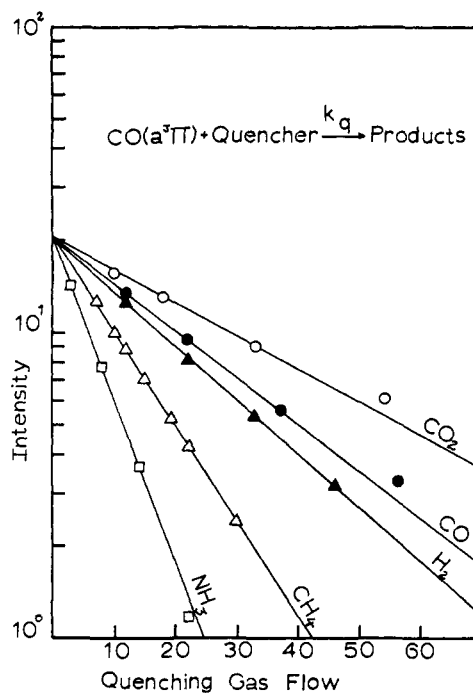


Figure 1. Plot of Cameron intensity, $CO(a^3\Pi \rightarrow X^1\Sigma^+)$, vs. concentration of quenching gas. The abscissa can be converted to concentration ($\text{molecules} (\text{cm}^3)^{-1}$) by multiplying the scale by the following constants: CO_2 , 3.70×10^{11} ; CO , 7.33×10^{10} ; H_2 , 6.86×10^{10} ; CH_4 , 8.33×10^{10} ; NH_3 , 1.46×10^{11} .

state, $H_2(b^3\Sigma_u^+)$, without change in internuclear distance requires 8.5 eV.¹² The $H_2(b^3\Sigma_u^+)$ curve is rather steep and, if the internuclear distance of H_2 increases from 0.9 Å (the outer turning point for $H_2(X^1\Sigma_g^+; v = 0)$) to 1.2 Å, the $H_2(b^3\Sigma_u^+)$ state could be reached with 6.5 eV of energy. Thus, the $CO(a^3\Pi)$ may release sufficient energy to produce the repulsive triplet state of H_2 by *nearly* vertical transitions for H_2 and for $CO(a)$. The quenching by the saturated hydrocarbon molecules probably can be rationalized by similar arguments involving the C-H bond. In contrast to $CO(a)$, $N_2(A)$ must undergo a strongly nonvertical process to be quenched by H_2 or saturated hydrocarbons with formation of their lowest triplet states. Since the first excited triplet state of CO_2 is bent, a vertical excitation from $CO_2(X^1\Sigma_g^+)$ to $CO_2(^3A)$ also may require a rather large amount of energy, thus partially explaining why CO_2 quenches $CO(a)$ faster than $N_2(A)$. Some additional support for the vertical-transition argument is the similarity in rate constants for some of the quenching molecules known to have low-lying acceptor states, *e.g.*, C_2H_4 and NO .

Although the vertical-transition argument is attractive, excessive emphasis probably should not be placed on it. For example, CO does quench $N_2(A)$ relatively efficiently and, since $CO(a)$ is the product, nearly all of the $N_2(A)$ energy is required. The other difference between $N_2(A)$ and $CO(a)$ is the large dipole¹³ moment [1.38 D (C^+O^-)] of the latter compared to zero dipole moment for $N_2(A)$. This may facilitate a charge-transfer mechanism for quenching of $CO(a)$ by hydrogen-containing molecules. The finding by

(12) W. Kolos and L. Wolniewicz, *J. Chem. Phys.*, **43**, 2429 (1965).

(13) (a) R. S. Freund and W. Klemperer, *ibid.*, **43**, 2422 (1965); (b) R. C. Stern, R. N. Gannon, M. E. Lesh, R. S. Freund, and W. A. Klemperer, *ibid.*, **52**, 3467 (1970).

Donovan and Hussain^{4b} of a rather efficient conversion of the electronic energy of CO($a^3\Pi$) to vibrational energy in CO(X) in the presence of H₂ suggests the lack of a chemical reaction leading to products which incorporate CO into their structure. Another argument against a chemical interaction for hydrogen is the very small isotope effect for quenching by deuterium (see Table I).

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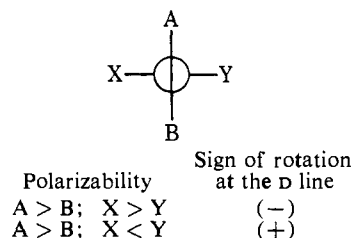
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The Absolute Configuration of (+)-1,2-Cyclononadiene¹

Sir:

Relatively few allenes of established absolute configuration are known and methods for determining configuration are fewer still.² Based on the original helical model of optical activity which Brewster proposed³ and has subsequently amplified,⁴ Lowe⁵ proposed the rule summarized below for predicting the absolute configuration of an allene from its rotation⁶ at the sodium D line and the relative polarizabilities of the substituents on the allenic linkage. For a 1,3-



dialkylallene, Lowe's rule predicts that the *R* enantiomer (A = X = R; B = Y = H) will be levorotatory. We note that Lowe⁵ was careful to restrict his rule to allenes with substituents "... which present no problems of conformational asymmetry."

1,2-Cyclononadiene (**1**), the smallest isolable cyclic allene, presents a most interesting system for consideration. While at first inspection **1** may appear to be a fitting case for application of Lowe's rule, further reflection makes evident the fact that the *allenic linkage induces dissymmetry into the methylene chain by re-*

(1) Acknowledgment is made to the National Science Foundation for support of this research (GP 25216).

(2) (a) For a review, see G. Krow, *Top. Stereochem.*, **3**, 31 (1970). Krow has assigned the incorrect configuration to (-)-**1** (pp 38-39) based on the assumption that the opening of the three-membered ring of the carbenoid precursor^{2b,14} occurred in the same sense as that found by Jones^{2c} for cyclopropylidenes leading to acyclic allenes. (b) W. R. Moore and R. D. Bach, *J. Amer. Chem. Soc.*, in press. (c) W. M. Jones and J. M. Walbrick, *Tetrahedron Lett.*, 5229 (1968), and references cited therein.

(3) J. H. Brewster, *J. Amer. Chem. Soc.*, **81**, 5475 (1959).

(4) J. H. Brewster, *Top. Stereochem.*, **2**, 33 (1967).

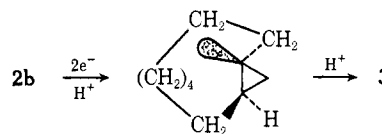
(5) G. Lowe, *Chem. Commun.*, 411 (1965).

(6) Following convention, subsequent designation of a compound as (+) or (-) refers to the rotation at the D line.

stricting it conformationally. Our suspicion that, as a consequence of this additional dissymmetry, the absolute configuration of **1** might not be predictable by Lowe's rule was increased on comparing the optical rotatory dispersion (ORD) and circular dichroism (CD) of **1** with the corresponding curves of allenes which lack conformational dissymmetry and thus should follow Lowe's rule. Thus, (+)-**1** shows a *positive* Cotton effect in the same region of the ultraviolet where (+)-1,3-dimethylallene^{7a} and (+)-1,3-di-*tert*-butylallene^{7a} show *negative* Cotton effects.^{7b}

Since the configuration of **1** is of interest with respect to both optical properties and mechanistic studies,^{2b} we sought to establish it in a way which, hopefully, would also develop principles of general significance. The method we now describe consists of a stereospecific addition, a stereospecific reduction, and a clear-cut ORD-CD correlation.

Addition of dibromocarbene to (+)-**1** gives the adduct **2a**.⁸ This addition can occur *only from the "outside" of the molecule* since the topology is such that the methylene chain effectively screens one side of each double bond (*i.e.*, the double bond of **2a** is *cis*). Reduction of **2a** with sodium in liquid ammonia with ether as a cosolvent and *tert*-butyl alcohol as a necessary proton donor gives (+)-*trans*-bicyclo[7.1.0]decane (**3**) as the main product along with some *cis*- and *trans*-cyclodecene.⁹ The *cis* isomer of **3** is not formed. This reaction must proceed by initial reductive replacement of the bromine atoms to give **2b**.¹⁰ Subsequent reduction of **2b** by a sequence of electron addition-protonation-electron addition must generate a *trans* carbanion as the immediate precursor of **3**. The re-



markable specificity indicates that a substantial thermodynamic preference for *trans* over *cis* substituents on a cyclopropane ring¹¹ is not diminished at the carbanion stage.¹²

This scheme establishes that **1**, **2**, and **3** are configurationally related as shown in the accompanying formulas. (Although absolute configurations are given, at this point only relative configurations are known.)

(7) (a) The ORD and CD measurements employed the (-)-enantiomers; (b) CD $\lambda_{\max}^{\text{benzene}}$ nm ($\Delta\epsilon$), (+)-**1**, 236 (1.2); (+)-1,3-dimethylallene, 223 (-0.6); (+)-1,3-di-*tert*-butylallene, 219 (-1.0). The $\Delta\epsilon$ values are not corrected for optical purity; P. Crabbe, A. F. Drake, S. F. Mason, H. W. Anderson, S. D. Clark, and W. R. Moore, *Chem. Commun.*, in press.

(8) Racemic **2a** has been described: W. R. Moore and T. M. Ozretich, *Tetrahedron Lett.*, 3205 (1967).

(9) These olefins appear to result from reduction of 1,2,3-cyclodecatriene formed by reductive opening of the three-membered ring.⁸

(10) Under these conditions **2b** is reduced to **3**. We have prepared racemic **2b** by reduction of racemic **2a** with tri-*n*-butyltin hydride and by application of the Simmons-Smith reaction to **1**.

(11) While experimental data are lacking, SCF-MO calculations have led to an estimate that *trans*-1,2-dimethylcyclopropane is 2.6 kcal/mol more stable than the *cis* isomer: N. C. Baird and M. J. S. Dewar, *J. Amer. Chem. Soc.*, **89**, 3966 (1967).

(12) The formally related reduction of derivatives of vinylidene-cyclopropane (R. W. Mills, R. D. H. Murray, and R. A. Raphael, *Chem. Commun.*, 555 (1971)) probably involves protonation of allylic (planar) carbanions from either side except when the protonation is intramolecular.