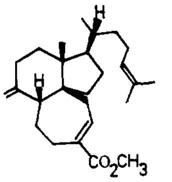
son.[26,27] *dl*-Methyl gascardate was converted into *dl*-gascardic acid (**22**) by saponification (NaOH, CH_3OH, THF, 12 h) completing the total synthesis.[28]

Since the assignment of stereochemistry at C-11 and C-14 has now been confirmed by the foregoing, the only remaining stereochemical question is the relative configuration at C-18.[8] It is interesting to note that the correlation of side-chain stereochemistry at C-20 encountered in the cholesterol–demosterol series[29] cannot be tested in this series. The natural methyl gascardate has the C-19 methyl signal essentially overlapping the C-19 methyl signal in the 18-epi isomer **23**. The expected trend in chemical shifts cannot be clearly observed in this series as it was in the previous studies by the Hoffmann-La Roche group.[29]



(23)

The configuration at C-6 is somewhat unexpected on the basis of Arigoni's studies; thus the mode of formation of the key acid cyclization product must now be reformulated in light of the structural and synthetic studies.[7,8] Our studies have now fully established the relative stereostructure of gascardic acid as **22**.

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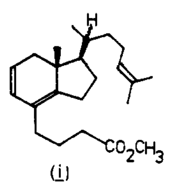
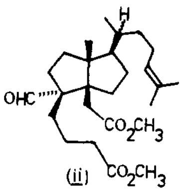


(i)



(ii)

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Intermolecular Energy Exchange of Infrared-Laser Excited $CHClF_2$ or SiF_4 with Br_2 at Excitation Energies of 70–200 kJ/mol[1]

Sir:

Intermolecular energy transfer at the high levels of vibrational excitation characteristic of reacting molecules is fundamental in chemical kinetics.[2] By use of pulsed infrared lasers, mean vibrational excitation energies of 100–200 kJ/mol of absorbing species in well-defined gas volumes are readily attained[3] in 300 ns or less. Consecutive energy transfer to a nonabsorbing species can then be measured if specific indicators of vibrational excitation are available.[4]

We report here preliminary studies of vibrational energy transfer from laser-excited $CHClF_2$ or SiF_4 to Br_2 in binary gas phase, using absorbance at 436 nm as an indicator of Br_2 vibrational excitation. The visible absorption of Br_2 is a well-known function of temperature[5-7] and can serve as a Br_2 vibrational thermometer: its features are reproduced by quantum-mechanical theory which neglects possible effects of translational and rotational excitation.[6-8] Absorbance by $CHClF_2$ and SiF_4 at 436 nm is nil.

Our kinetic results, interpreted in this way, indicate that energy transfer proceeds according to mechanism 1, where *A* denotes the IR absorbing component ($CHClF_2$ or SiF_4) and *B* denotes Br_2. *V* denotes vibrational energy and *W* translation/rotational energy. Direct $V_A - V_B$ transfer appears to be relatively unimportant.

$$V_A \overset{1/\sigma}{\rightleftharpoons} W(\mathrm{T/R,\ gas}) \overset{1/\tau}{\rightleftharpoons} V_B \qquad (1)$$

Table I. Kinetic Analysis of Energy Transfer According to Mechanism 1

no.	c_A,[a] mM	c_B,[a] mM	E_{abs}, kJ/(mol A)	θ, K	$T_{B,\infty}$, K	$10^{-6}\sigma^{-1}$, s^{-1}	$\sigma^{-1} c_{A,eff}^{-1}$, $s^{-1} M^{-1}$	$\tau^{-1} c_{B,eff}^{-1}$, $s^{-1}M^{-1}$ [b]
				$CHClF_2$–Br_2				
1	0.370	0.312	74	1070	1100	0.91	1.25×10^9	1.1×10^9
2	3.82	0.764	127	1770	(1700)	3.5	0.75×10^9	0.5×10^9
3	0.294	0.547	87	1000	1050	0.86	1.37×10^9	1.8×10^9
4	0.294	0.495	125	1310		1.05	1.22×10^9	1.0×10^9
5	3.69	1.27	103	1470	1400	4.1	0.80×10^9	1.3×10^9
				SiF_4–Br_2				
6	0.64	2.15	197	1370	1260	>25	$>8 \times 10^9$	0.8×10^9

[a] Effective total concentrations for kinetic analysis of energy transfer were estimated according to the SSH model:[14] $c_{A,eff} = c_A + (\mu_{AB}/\mu_{AA})^{1/2}c_B$, $c_{B,eff} = c_B + (\mu_{AB}/\mu_{BB})^{1/2}c_A$, where μ denotes the reduced mass of the collision complex. [b] At 1100 K.

$CHClF_2$–Br_2. Typical oscilloscope records of absorbance at 436 nm and IR pulse intensity at 1088 cm^{-1} are traced in Figure 1. There is a time lag preceding the change in absorbance, especially at the lower pressure, which indicates that the rise in the vibrational temperature T_B of Br_2 is preceded by some other process.[9] We believe that process to be $V_A - T/R$ relaxation for two reasons. (a) The plateau temperature $T_{B,\infty}$ reached by Br_2 after 2-5 μs is essentially the thermal equilibrium temperature θ. The latter is calculated from the amount of energy absorbed from the IR pulse, for a constant-volume system. This shows that the T/R modes share the absorbed energy. (b) Kinetic analysis according to mechanism 1 yields values of the expected magnitude for $1/\tau$.

Results of the kinetic analysis are listed in Table I. (Chemical reaction, which would cause error in predicting temperature, is absent in experiments 1, 3, and 6 and insignificant on the given time scale in 4 and 5, but may be significant in 2.) The basic equations are 2-4. T denotes the T/R temperature, V_A^e and V_B^e are values of V_A and V_B at thermal equilibrium at temperature T, E_{abs} is the energy absorbed per mole of A from the IR pulse at time t, and x denotes mole fraction.[15]

$$dV_A/dt = (dE_{abs}/dt) - [(V_A - V_A^e)/\sigma] \qquad (2)$$

$$\frac{dV_B}{dt} = -(V_B - V_B^e)/\tau \qquad (3)$$

$$\frac{dW}{dt} = (3x_A + {}^5\!/\!_2 x_B)R(dT/dt)$$
$$= x_A[(V_A - V_A^e)/\sigma] + x_B\,[(V_B - V_B^e)/\tau] \qquad (4)$$

The data obtained in any single experiment were sufficient for fitting two parameters. One of these was σ, which was assumed constant. The other was τ at 1100 K. Because these processes are collisional, $(c\sigma)^{-1}$ and $(c\tau)^{-1}$ are analogues of rate constants (c = molar concentration). Following Millikan and White,[10] the temperature dependence of $(c\tau)^{-1}$ was represented by

$$(c\tau)^{-1} = BT\exp(-AT^{-1/3}) \qquad (5)$$

Parameters A and B were obtained by fitting the known value of $(c\tau)^{-1}$ at 400 K[11] and adjusting the 1100 K value for least-squares fit. As shown in Table I, the average $(c\tau)^{-1}$ at 1100 K obtained in this way is 1.0×10^9 M^{-1} s^{-1}, with a standard error (se) factor of 1.5. By comparison, extrapolation of ultrasonic data obtained at 300-600 K to 1100 K gives 7.4×10^8 s^{-1} M^{-1}, with an se factor of 2.

The mean value of $(c\sigma)^{-1}$ for $CHClF_2$ is 1.1×10^9 s^{-1} M^{-1}, with an se factor of 1.3, at an average temperature of ~700 K. By comparison, the ultrasonic value of $(c\sigma)^{-1}$ at 300 K is 2.6×10^8 s^{-1} M^{-1}.[12]

SiF_4–Br_2. Results of a single experiment are listed in Table I. The value of $(c\tau)^{-1}$ is in the range of the previous values, in support of the assumed mechanism. The value of $(c\sigma)^{-1}$ is too great to be measured with our instrumentation. A lower limit of 8×10^9 s^{-1} M^{-1} is indicated.

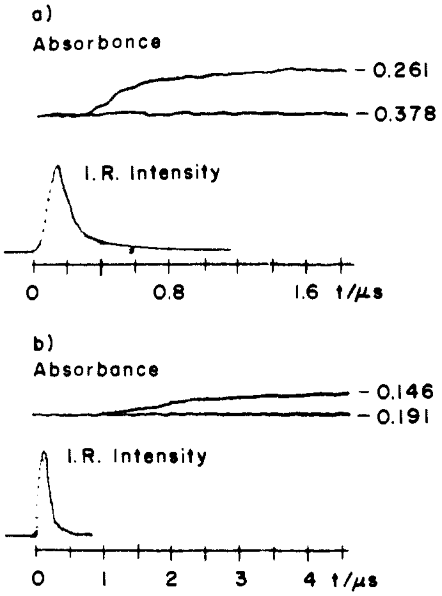

Figure 1. Tracings of oscilloscope records of absorbance at 436 nm and IR pulse intensity at 1088 cm^{-1} for $CHClF_2$-Br_2 gas mixtures: (a) Table I, No. 5; (b) Table I, No. 3. Both properties are recorded with light electrical filtering (time constant, 30 ns). Synchronization of the two properties is accurate to ~20 ns. The rising curve of the laser pulse triggers the oscilloscope. In the kinetic calculations, the 30-ns response time of the photomultiplier circuit was allowed for.

Our results lend additional support to the hypothesis[13] that, at high excitation, a constant *fraction* of the excess vibrational energy [$(V - V^e)$ in eq 2-4] is removed per collision. The magnitude of this fraction apparently may vary widely. It is ~0.1% for $CHClF_2$ and $\gtrsim 1\%$ for SiF_4.

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Oxidation of CO to CO_2 by Ni–NO_2 Complexes: a Mechanistic Study[1]

Sir:

The oxidation of carbon monoxide by nitrite is a thermodynamically favored,[2] but kinetically slow,[3] process in the absence of transition metal complexes. However, when complexes of nickel, iron, cobalt, ruthenium, rhodium, or iridium are present, carbon monoxide reacts readily with nitrite forming carbon dioxide and the corresponding transition metal-nitrosyl complex.[4] The present kinetic study was undertaken to explore the specific role played by transition metal complexes in promoting the oxidation of carbon monoxide by nitrite.

The nickel complexes, $Ni(NO_2)_2L_2$, were selected for these investigations. In their report of the reaction between $Ni(NO_2)_2(PEt_3)_2$ and CO, Booth and Chatt[4a] found that the reaction was rapid at ambient conditions and produced the reduced nickel-nitrosyl complex, $Ni(NO)(NO_2)(PEt_3)_2$, in good yield. However, these authors also found this $\{NiNO\}^{10}$ product[5] to be air sensitive and difficult to purify. Although CO_2 was presumed to be the oxidized product, it was not identified in the reaction mixtures. Consequently, several $Ni(NO_2)_2L_2$ complexes have been prepared and their reactions with CO examined.[6] Among these complexes, $Ni(NO_2)_2(DPPE)$[7] has the combination of solubility, reaction rates, and ease of product isolation most suited for the initial studies reported here.

The reaction of $Ni(NO_2)_2(DPPE)$ with carbon monoxide in dry, oxygen-free dichloromethane produced a deep purple solution from which a dark blue microcrystalline complex, $Ni(NO)(NO_2)(DPPE)$, was isolated in nearly quantitative yield. The compound was characterized by elemental analysis and IR and visible-UV spectroscopy.[8a] The CO_2 evolved in this reaction was identified by IR spectroscopy and gas chromatography and analyzed by standard vacuum line techniques.[8b] The stoichiometry corresponds to reaction 1:

$$CO + Ni(NO_2)_2(DPPE) \xrightarrow{CH_2Cl_2} CO_2 + Ni(NO)(NO_2)(DPPE) \quad (1)$$

No evidence for nickel species other than those in reaction 1 was obtained from spectroscopic examination of the reacting solutions.

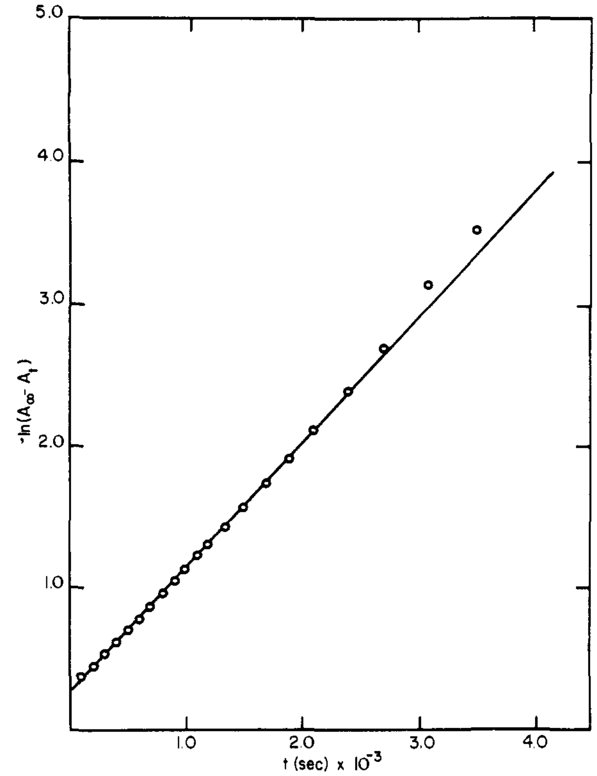

Figure 1. Plot of $-\ln(A_\infty - A_t)$ vs. *t* at 570 nm for the reaction of $Ni(NO_2)_2(DPPE)$ with CO in CH_2Cl_2 at 20.0 °C.

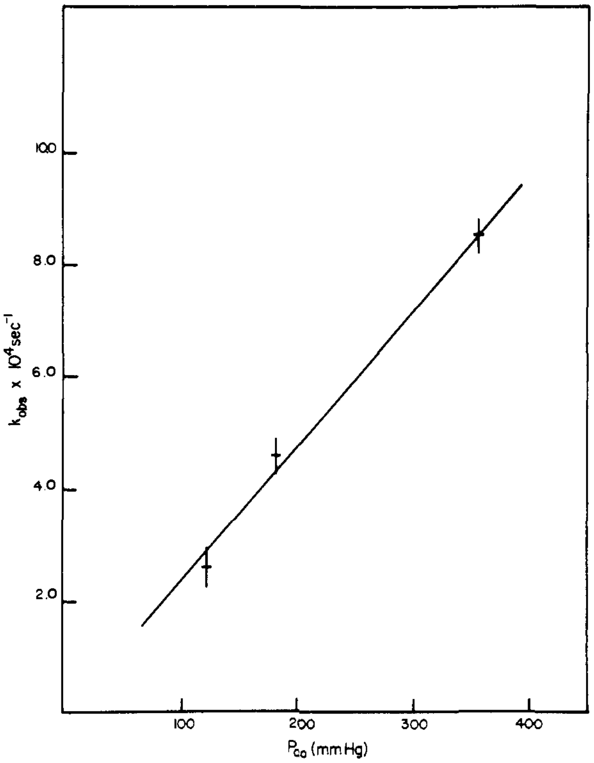

Figure 2. Dependence of k_{obsd} on p_{CO} (20.0 °C, CH_2Cl_2) for the reaction of $Ni(NO_2)_2(DPPE)$ with CO.

The kinetic features of this reaction in CH_2Cl_2 were obtained at 20 °C by following the appearance of the absorption band of the $\{NiNO\}^{10}$ product at 570 nm. The reaction rate was determined at several pressures with CO present in a three- to tenfold excess. Under these conditions, the reaction is first order in $Ni(NO_2)_2(DPPE)$, while k_{obsd} is linearly dependent upon p_{CO} (Figures 1 and 2). The overall reaction is second order, and there is no evidence for a first-order term in the rate law, since, within experimental error, the plot of k_{obsd} vs. p_{CO}

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