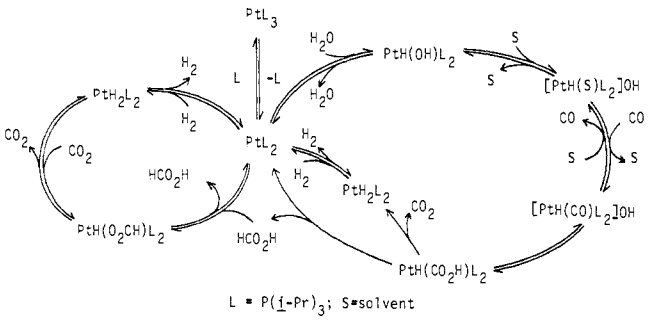
Scheme I. Possible Mechanism for the Water Gas Shift Reaction Catalyzed by $Pt[P(i\text{-}Pr)_3]_3$



yield) by the reaction of *trans*-{PtH(CO)[P(*i*-Pr)$_3$]$_2$}BPh$_4$ with CH_3ONa at room temperature. Facile formation of Pt(R)-(CO_2H)(diphos) from Pt(R)(OH)(diphos) (R = CH_3, c-C_6H_9) is also known.[17]

The CO_2 evolution should occur from thermal decomposition[18] of the unstable $PtH(CO_2H)L_2$.[19] A dihydride species *trans*-$PtH_2[P(i\text{-}Pr)_3]_2$[20] (**4**) will then be formed. The reaction of **4** with CO leading to $Pt_3(CO)_3L_4$ is possible. However, this route in the catalysis is excluded since the isolated $Pt_3(CO)_3[P(i\text{-}Pr)_3]_4$[21] was found almost inactive catalytically. Thus, **4** is thought to undergo hydrogen elimination (Scheme I). Involvement of **4** in the catalytic cycle was confirmed by the dihydride-catalyzed water gas shift reaction[23] from which was isolated **3** as its BPh_4 salt.

Alternatively, reductive elimination of HCO_2H from $PtH(CO_2H)L_2$ with concomitant formation of $Pt[P(i\text{-}Pr)_3]_2$ is possible. A rapid catalytic decomposition of HCO_2H into CO_2 and H_2 occurs with **1** at room temperature,[24] and the platinum complex was recovered as **4** quantitatively. The decomposition of HCO_2H probably proceeds through oxidative addition of HCO_2H to give *trans*-$PtH(O_2CH)[P(i\text{-}Pr)_3]_2$, which is followed by β-hydrogen elimination affording **4** and CO_2. Consistent with this, the decomposition of HCO_2H was also catalyzed by *trans*-$PtH(O_2CH)[P(i\text{-}Pr)_3]_2$[25] prepared separately by CO_2 insertion into the Pt-H bond of **4**. The possible pathways are summarized in Scheme I.

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(9) BF_4^- salt: ν(Pt-H) 2230 cm^{-1}; δ −18.9 (Pt-H, t, $J_{P\text{-}H}$ = 14.2, $J_{Pt\text{-}H}$ = 1005 Hz), 1.20 (CH_3, q, $^3J_{P\text{-}H} + {}^5J_{P\text{-}H}$ = 14.7, $J_{H\text{-}H}$ = 7.3 Hz), ~2.1 (CH, m), 7.0 ~8.3 and 8.70 (pyridine, m).
(10) ν(Pt-H) 2178, ν(CO) 2058 cm^{-1}; δ −4.55 (Pt-H, t, $J_{P\text{-}H}$ = 11.3, $J_{Pt\text{-}H}$ = 881 Hz), 1.32 (CH_3, q, $^3J_{P\text{-}H} + {}^5J_{P\text{-}H}$ = 15.0, $J_{H\text{-}H}$ = 7.5 Hz), ~2.7 (CH, m).
(11) K_{diss} = 1.4 × 10^{-1} M (20 °C) in THF, which was determined by the electronic spectra with and without added P(*i*-Pr)$_3$. Two isosbestic points were observd at 363 and 374 nm.
(12) The pH_{app} of NaOH (9.8 × 10^{-3} M) measured in aqueous pyridine ([H_2O] = 22.2 M) at 20 °C is 13.5.
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(15) ν(Pt-H) 1943, ν(CO) 1575 cm^{-1}; δ −9.16 (Pt-H, t, $J_{P\text{-}H}$ = 17.6, $J_{Pt\text{-}H}$ = 609 Hz), 1.23 (CH_3, q, $^3J_{P\text{-}H} + {}^5J_{P\text{-}H}$ = 14.2, $J_{H\text{-}H}$ = 7.1 Hz), ~2.3 (CH, m).
(16) ν(Pt-H) 1985, ν(CO) 1617, ν(C-O) 1008 cm^{-1}; δ −8.98 (Pt-H, t, $J_{P\text{-}H}$ = 17.7, $J_{Pt\text{-}H}$ = 630 Hz), 1.17 (CH_3, q, $^3J_{P\text{-}H} + {}^5J_{P\text{-}H}$ = 14.0, $J_{H\text{-}H}$ = 7.0 Hz), ~2.1 (CH, m), 3.67 (CH_3O, s, $J_{Pt\text{-}H}$ = 4.5 Hz).
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(19) The decomposition of *trans*-$PtH(CO_2K)[P(i\text{-}Pr)_3]_2$ occurred above 70 °C.
(20) T. Yoshida and S. Otsuka, *J. Am. Chem. Soc.*, **99**, 2134–2140 (1977).
(21) ν(CO) 1840 (w), 1770 (vs) cm^{-1}; δ 1.17 (CH_3 dd, $J_{H\text{-}P}$ = 13.5, $J_{H\text{-}H}$ = 7.0 Hz), ~2.5 (CH, m). The equivalence of four P(*i*-Pr)$_3$ units may be ascribed to the ligand dissociation as observed for $Pt_3(CO)_3(PPh_3)_4$.[22]
(22) J. Chatt and P. Chini, *J. Chem. Soc. A*, 1538–1542 (1970).
(23) The water gas shift reaction catalyzed by **4** under the same conditions (in acetone, 100 °C) shown in the text produced 46 mol of H_2 and 40 mol of CO_2/mol of catalyst.
(24) Employing $Pt[P(i\text{-}Pr)_3]_3$ (0.1 mmol) in a mixture of acetone (15 mL) and H_2O (1 mL), HCO_2H (5 mmol) decomposed at 20 °C with a half-time of 15 min.
(25) ν(Pt-H) 2200, ν(OCO) 1530, 1310 cm^{-1}; δ −21.8 (Pt-H, t, $J_{P\text{-}H}$ = 14.8, $J_{Pt\text{-}H}$ = 1012 Hz), 1.33 (CH_3, q, $^3J_{P\text{-}H} + {}^5J_{P\text{-}H}$ = 14.0, $J_{H\text{-}H}$ = 6.8 Hz), ~2.4 (CH, m), 9.5 (O_2CH, br). The platinum(II) hydrido formate complex has a precedent, *trans*-$PtH(O_2CH)[P(c\text{-}C_6H_{11})_3]_2$: A. Immirzi and A. Musco, *Inorg. Chim. Acta*, **22**, L35–L36 (1977).

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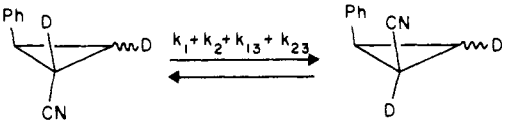
Complete Kinetic Analysis of Thermal Stereomutations of (+)-(1*S*,2*S*,3*S*)-*r*-1-Cyano-*t*-2-phenyl-1,*c*-3-dideuteriocyclopropane

Sir:

Both one-center (k_i) and two-center (k_{ij}) thermal epimerizations of cyclopropanes are known in special cases,[1-3] but there is no reliable method for anticipating the relative importance of these reaction modes in other cyclopropyl systems. Only experiments capable of discriminating among all one-center and all two-center epimerization possibilities can provide the factual grounds for developing theory appropriate to this task.

To synthesize the substrate selected for our kinetic studies, (+)-(1*S*,2*S*,3*S*)-*r*-1-cyano-*t*-2-phenyl-1,*c*-3-dideuteriocyclopropane ((+)-**1**-*c*), *trans*-β-deuteriostyrene,[4] and ethyl diazoacetate-d_1[5] were reacted in the presence of $CuSO_4$; the resultant mixture of esters was epimerized with potassium *tert*-butoxide in deuterated *tert*-butyl alcohol[6] to afford *r*-1-ethoxycarbonyl-*t*-2-phenyl-1,*c*-3-dideuteriocyclopropane. Hydrolysis with dilute acid and resolution through the quinine salt[7] gave (+)-(1*S*,2*S*,3*S*)-2-phenyl-1,3-dideuteriocyclopropanecarboxylic acid. Conversion to the corresponding nitrile, (+)-**1**-*c*, was accomplished by way of the acid chloride and the amide.[8] Epimerization of (+)-**1**-*c* with potassium *tert*-butoxide in deuterated *tert*-butyl alcohol gave a 70:30 mixture of (+)-**1**-*c* and (−)-**2**-*t*, without racemization of (+)-**1**. The rotations in $CHCl_3$ of optically pure nitriles were $[\alpha]_D$ +369° for (+)-**1** and $[\alpha]_D$ −22.8° for (−)-**2**.

Thermal equilibration[9] at 242.1 °C of **1** and its cis isomer **2**, starting with either isomer, was followed by VPC; the concentration vs. time data provided values for the rate constant $(k_1 + k_2 + k_{13} + k_{23}) = 1.09 \times 10^{-5}$ s^{-1} and the equilibrium constant $K = 0.40$.



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When the thermal isomerizations of **1**-*c* and of **2**-*t* were examined by VPC analysis, followed by preparative VPC separation of cis and trans isomers and NMR analysis to distinguish **1**-*c* from **1**-*t*, and **2**-*c* from **2**-*t*, the concentration vs. time data—44 experimental points—were fit to theoretical curves based on exact solutions to the kinetic expressions ap-

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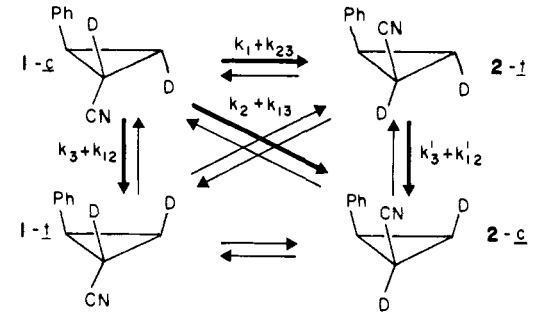
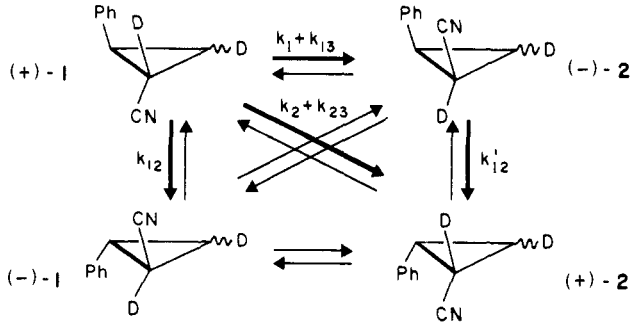
Scheme I



Scheme II



propriate to Scheme I and the parameters K, $(k_1 + k_{23}) = 0.76 \times 10^{-5}\ s^{-1}$, $(k_2 + k_{13}) = 0.33 \times 10^{-5}\ s^{-1}$, $(k_3 + k_{12}) = 0.60 \times 10^{-5}\ s^{-1}$, and $(k_3' + k_{12}') = 0.43 \times 10^{-5}\ s^{-1}$. The eight rate constants not given explicitly in Scheme I are derivable from these five parameters and the principle of microscopic reversibility. Calculated concentrations matched observed concentrations of **1**-*c*, **1**-*t*, **2**-*t*, and **2**-*c* with an average deviation of 0.8 mol %.

If the thermal isomerization of (+)-**1** (or (−)-**2**) were analyzed by VPC, followed by VPC separation of cis and trans isomers and polarimetric analysis of each combination of enantiomers, application of the same exact equations would lead to experimental values for $(k_1 + k_{13})$, $(k_2 + k_{23})$, k_{12}, and k_{12}' (Scheme II).

Although six experimental values would then be available for isomerizations from a single starting material such as (+)-**1**-*c*, and there are six rate constants to be deduced, the kinetic problem would not be solved; values of k_{12}, k_3, $(k_1 + k_{23})$, $(k_2 + k_{13})$, $(k_1 + k_{13})$, and $(k_2 + k_{23})$ would be available, and additional experimental data would be required to overcome the linear dependency of the four sums of two rate constants.

Analysis of samples derived from kinetic runs starting from (+)-**1**-*c* through NMR spectroscopy with the aid of the optically active shift reagent tris[3-(heptafluoropropylhydroxymethylene)-*d*-camphorato]europium(III)[10] provided the new data required. In its presence, the enantiotopic protons C(3) H in **1**-*t* and **2**-*t* can be distinguished: the more downfield of the two C(3) H doublets is due to the (+) isomer of **1**-*t* and the (−) antipode of **2**-*t*.

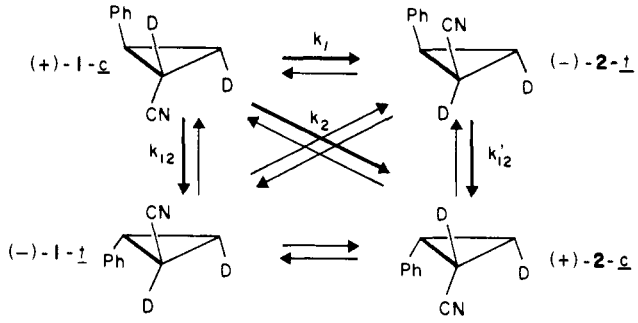
The cis products from (+)-**1**-*c* were found to contain (−)-**2**-*t* but not (+)-**2**-*t*, and therefore $k_{23} = 0$. This, together with the observed rotation of **2** and the NMR-determined ratio of **2**-*t* to **2**-*c*, implied that the concentration of (−)-**2**-*c* in the product mixture was zero, within likely experimental error; hence $k_{13} = 0$. When the trans isomer recovered from a kinetic run was examined with the aid of the optically active shift reagent, the C(3) H doublet from (+)-**1**-*t* was so small it could be ascribed to the stereochemical impurity of the starting material, which suggested that $k_3 = 0$. Finally, the trans material recovered from kinetic runs and then epimerized at C(1) with KOBu-*t*/DOBu-*t* afforded (−)-**2**-*t* but no (+)-**2**-*t*; thus k_{123}, the triple

Table I. Calculated[a] and Observed Mole Percent Concentrations of the Cyclopropane Isomers of Scheme III

Time, min	(+)-**1**-*c*	(−)-**1**-*t*	(−)-**2**-*t*	(+)-**2**-*c*
	NMR Data			
0	98.7	1.3	0	0
240 (calcd)	79.1	8.8	8.1	4.0
240 (exptl)	78.5	8.7	8.6	4.1
0	95.5	4.5	0	0
375 (calcd)	69.2	14.3	10.6	5.9
375 (exptl)	68.4	14.3	10.9	6.4
	Rotational Data			
0	96.7	3.3	0	0
240 (calcd)	78.8	9.1	8.1	4.0
240 (exptl)	78.8	8.4	8.7	4.0
0	100	0	0	0
375 (calcd)	71.9	11.6	10.8	5.7
375 (exptl)	70.1	12.5	11.7	5.7

[a] According to Scheme III and the parameters $K = 0.40$, $k_1 = 0.76 \times 10^{-5}\ s^{-1}$, $k_2 = 0.33 \times 10^{-5}\ s^{-1}$, $k_{12} = 0.60 \times 10^{-5}\ s^{-1}$, and $k_{12}' = 0.43 \times 10^{-5}\ s^{-1}$.

Scheme III



epimerization process in the thermal rearrangement, is, as expected,[3c] not competitive, and indirect routes from (+)-**1**-*c* to (−)-**1**-*c* are not effective.

If k_3, k_{13}, k_{23}, and k_{123} are indeed 0, then the stereomutations of the 1-cyano-2-phenyl-1,3-dideuteriocyclopropanes involve just four isomers, not eight, and kinetic Scheme III applies.

To test the adequacy of Scheme III quantitatively, two samples of (+)-**1**-*c* were isomerized and the experimentally observed concentrations of the four isomers as derived by NMR data, and as derived from optical rotation data, were compared with calculated concentrations (Table I). The agreement between experimental and calculated concentrations supports the formulation of Scheme III.

These results support the oft employed assumption that the stereomutations of a cyclopropane such as **1** would proceed through k_1, k_2, and k_{12} processes alone.[11] Uncertainties in interpretation of data for *trans*-dialkenylcyclopropanes[12] and 1-cyano-2-isopropenylcyclopropane[11g] caused by reports of the dominance of k_{ij} processes in 1,2-dideuteriocyclopropane[3a] and 1-phenyl-2-deuteriocyclopropane[3b,c] are thereby diminished.

Acknowledgement. This work was supported by the National Science Foundation.

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Generation of Singlet Oxygen in the Reaction of Superoxide Anion Radical with Diacyl Peroxides[1]

Sir:

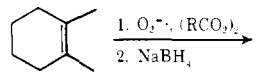
There has been considerable debate recently regarding the formation of singlet molecular oxygen from superoxide anion radical, O_2^{-}.[2] We wish to report the apparently efficient production of singlet oxygen in the reaction of $O_2^{-}\cdot$ with the oxidizing agents benzoyl peroxide and lauroyl peroxide. These experiments involved the addition of a solution of the diacyl peroxide in benzene to a slurry consisting of KO_2 and 18-crown-6 in benzene. The corresponding carboxylic acids[3] were isolated in quantitative yield in accordance with the stoichiometry shown in eq 1.

$$2O_2^{-}\cdot + RCOOCR \longrightarrow 2O_2 + 2RCO_2^{-} \qquad (1)$$

The following observations suggest that a significant fraction of the oxygen generated in these systems is in the excited singlet state, presumably $^1\Delta_g$.

A. Trapping Experiments. Reaction of $O_2^{-}\cdot$ with benzoyl peroxide or lauroyl peroxide in the presence of a slight excess of the common singlet oxygen trap 1,3-diphenylisobenzofuran, **1**, was found to produce 2 equiv of *o*-dibenzoylbenzene, **2**, per equivalent of peroxide. The yields of **2** determined by ultraviolet spectroscopy were found to be >97% in both systems; isolated yields of **2** from $O_2^{-}\cdot$ benzoyl peroxide averaged 86% for three trials. Trapping experiments were also conducted with tetramethylethylene[5] to produce 3-hydroxy-2,3-dimethyl-1-butene in low yield.

Since there is evidence[6,7] that these commonly utilized scavengers may not be unambiguous as detectors of singlet oxygen, we investigated the reaction of $O_2^{-}\cdot$ with benzoyl peroxide or lauroyl peroxide in the presence of 1,2-dimethylcyclohexene, **3**. This compound has been shown[5] to distinguish between oxidation by singlet oxygen and a simple free-radical autoxidation reaction on the basis of a distinctly different distribution of products for the two processes. Under our conditions in the reaction of $O_2^{-}\cdot$ and benzoyl peroxide, **4, 5,** and **6** (eq 2) were formed in relative yields of 92, 5, and 3%, respectively, demonstrating the generation of singlet oxygen in this system. When lauroyl peroxide was used as the substrate, the relative yields were found to be 77, 18, and 5%, respectively. Simple free-radical autoxidation of **3** by triplet molecular oxygen catalyzed by di-*tert*-butyl peroxide produced a ratio for **4, 5,** and **6** of 16, 7, and 77%, respectively. The predominance of **6** in radical autoxidation but its production in low yield in the $O_2^{-}\cdot$ and peroxide experiments is indicative of the intermediacy of singlet oxygen in the latter.[5] Control experiments indicated that **1** and **3** were unreactive toward KO_2, benzoyl peroxide, or lauroyl peroxide separately. Likewise, controls with KOH, crown ether, and molecular oxygen demonstrated no reaction with **1** or **3**; KOH, crown ether, and dibenzoyl peroxide underwent only slow reactions with these singlet oxygen traps which could not effectively compete with the rapid reaction with KO_2.



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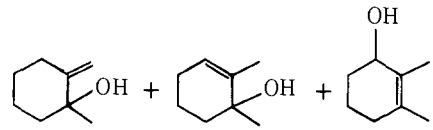

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B. Oxygen Evolution. When reactions of $O_2^{-}\cdot$ were carried out in the presence of **1**, the amount of oxygen liberated was found to be dependent upon the amount of **1** used; oxygen evolution was suppressed completely with excess **1**. Although oxygen evolution could never be completely inhibited by less efficient singlet oxygen traps[8] such as tetramethylethylene or **3**, a decrease in the amount of oxygen evolved was observed.

C. Quenching of Singlet Oxygen by Superoxide. The rate constant for quenching of singlet oxygen by $O_2^{-}\cdot$ has been determined[2b] to be $1.6 \times 10^9\ M^{-1}\ s^{-1}$. This suggests that $O_2^{-}\cdot$ should compete with even efficient singlet oxygen traps such as **1** while slower reacting olefinic and other traps should be less effective in our system compared to other methods of generating singlet oxygen. We found this to be the case with **1, 3,** and tetramethylethylene; the latter two scavengers produced the singlet oxygen product in comparitively low yields. Additional substantiation that $O_2^{-}\cdot$ competes with **1** for singlet oxygen was obtained when experimental conditions were varied in the reaction of benzoyl peroxide with $O_2^{-}\cdot$ in the presence of **1**. It was found that the yield of **2** depended logically upon the following three factors: (i) the amount of KO_2 used, (ii) the concentration of 18-crown-6, and (iii) and concentration of **1**.[9] Increasing the amounts of either KO_2 or crown ether resulted in lower yields of **2** while increasing the concentration of **1** produced higher yields of the singlet oxygen product.

D. Quenching of Singlet Oxygen by β-Carotene. When the reaction of benzoyl peroxide with $O_2^{-}\cdot$ was carried out in the presence of both **1** and β-carotene, the yield of **2** was found to depend upon the amount of β-carotene, a known quencher of singlet oxygen.[10] Moreover, the amount of **2** produced was qualitatively in accord with the respective rate constants for trapping by **1** and quenching by β-carotene.

Our results indicate that singlet oxygen or some species mimicking singlet oxygen[2a,11] can be efficiently produced by the reaction of $O_2^{-}\cdot$ with diacyl peroxides, although the mechanism of production is only speculative at present. It is possible that many of the deleterious effects on metabolic systems which have been attributed to $O_2^{-}\cdot$ or HO· may actually be due to singlet oxygen produced by oxidation of $O_2^{-}\cdot$ with biological oxidizing agents. This hypothesis is particularly attractive since there is now a consensus that the Haber-Weiss reaction between $O_2^{-}\cdot$ and H_2O_2 to generate HO· is too slow to be of significance in biological systems.[7]

Additional work on the reaction of $O_2^{-}\cdot$ with other oxidizing agents is in progress.

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