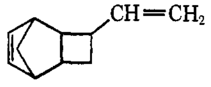
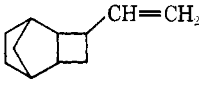
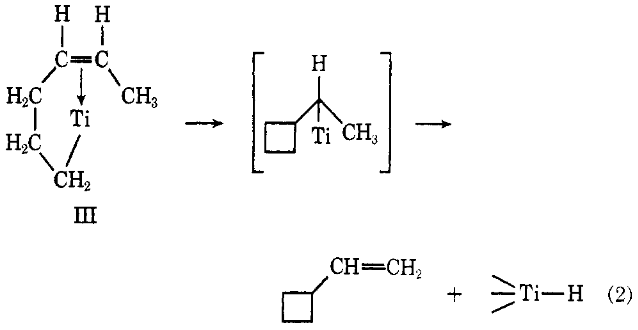
$(CH_2Ph)_3$. Piperylene–ethylene codimers were 64% cyclics, *cis*- and *trans*-1-methyl-2-vinylcyclobutane (52%) and *n*-propenylcyclobutane (12%), accompanied by 3-methyl-*cis*-1,4-hexadiene as the other principal product. However, isoprene–ethylene gave only 2-methyl-*n*-hexadienes (96%) and 3-methyl-*n*-hexadienes (4%) as codimers. Propylene did not codimerize with butadiene. But the strained olefins, norbornadiene and norbornene, reacted with butadiene to give I and II, respectively, in high yields (~90% of the codimer). The same butadiene–norbornadiene codimer I has recently been reported with Fe and Mn catalysts.[9]


I


II

Two mechanistic schemes appear possible for ethylene–butadiene cyclodimerization, one wherein the cyclic and open-chain codimers (vinylcyclobutane and hexadienes) have a common intermediate or an alternative wherein they do not. Metal hydride mechanisms have been proposed for the codimerization of ethylene and butadiene to hexadienes by group VIII metals[2a, 2i] and for ethylene dimerization by homogeneous titanium catalysts.[10] Addition of butadiene to a titanium hydride species followed by ethylene would lead to III, a common intermediate, which could give *cis*-1,4-hexadiene by β elimination or vinylcyclobutane by an intramolecular addition–elimination with regeneration of titanium hydride (eq 2). Alternatively, a [2 + 2] cycloaddition mechanism could be proposed for vinylcyclobutane with no common intermediate or movement of hydrogens. The present data do not allow a clear choice between these or other mechanisms. But it does appear easier to account for the observed ethylene codimers with isoprene or piperylene by intermediates analogous to III than by a [2 + 2] cycloaddition.



III

(2)

Acknowledgments. Special acknowledgments are given to Dr. W. Keim and Dr. J. E. Mahler for helpful discussions and to Mr. S. D. Siegel for technical assistance.

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Received May 30, 1972

Detection of Steady-State Free-Radical Concentrations by Photoionization

Sir:

The observation of free radicals in ordinary gas-phase reactions is difficult as their steady-state concentrations are very low.[1,2] Only in a few especially favorable reactions have these radical concentrations been measured directly.[3,4] Ionization potentials of free radicals are usually lower than those of the parent molecule, and thus, in principle, radicals can be preferentially ionized. Conventional electron-impact ionization is not well suited to radical detection because of low cross sections near the threshold, interference by fragmentation of larger molecules, and cracking on the hot filament.[5] The use of monochromatic light sources makes photoionization extremely selective. If the energy of the photoionizing quantum is only slightly greater than the ionization potential of a particular intermediate, then no subsequent fragmentation occurs.[6,7]

A photoionization mass spectrometer has been constructed by combining a quadrupole mass filter with argon, krypton, and xenon vacuum-ultraviolet resonance lamps.[8] Reactants from a conventional flow system were sampled through a pinhole inlet into the mass spectrometer where ions were produced by photoionization.[9] Free radicals have been detected during the oxidation of several simple hydrocarbons. Each free radical was uniquely assigned from its mass to charge ratio, with both normal and deuterated fuel, and from limits on its ionization potential obtained by alternating between the several lamps. Oxygen atoms were produced, in the absence of molecular oxygen, by titrating nitrogen atoms with nitric oxide. Scans of the reactants individually showed no detectable fragmentation and no interfering impurities. Concentrations and reaction times were selected to ensure that the oxygen atom and fuel concentrations were close to their initial values (within 15%) for all experiments.

The addition of oxygen atoms to methane produced signals at mass 30, identified as CH_2O, mass 29 (CHO), and mass 15 (CH_3). The time dependence of these products is shown in Figure 1. (CD_4 was used when investigating the formaldehyde peak in order to avoid interference from traces of NO at mass 30.) The $[CD_2O]$ increased linearly with reaction time, as expected for a stable product. The reaction of oxygen atoms with formaldehyde is too slow to be significant except possibly at the longest contact times.[10] The constant signals at mass 29 and 15 indicate that concentrations of these radicals had attained their steady-state values, $[CHO]_{ss}$ and $[CH_3]_{ss}$, respectively. The $[CH_3]_{ss}$ suggests that the rate of methyl radical formation, in the generally accepted first step,[11] reaction 1,

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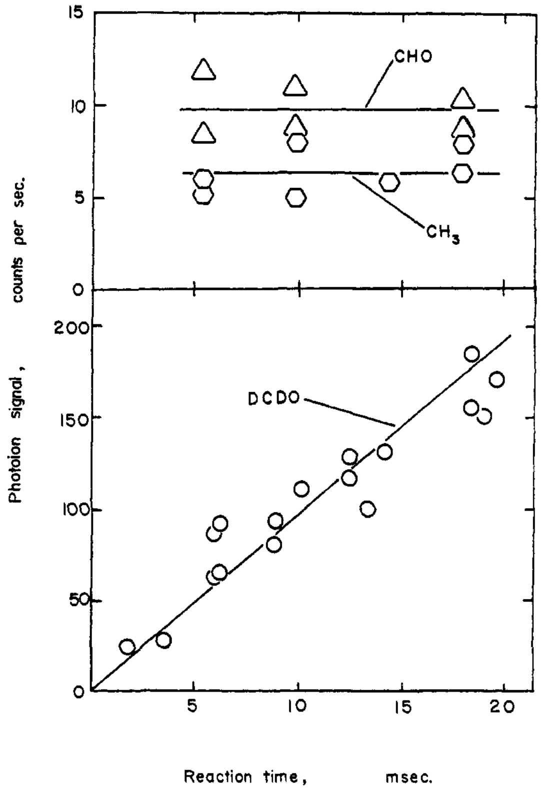

Figure 1. Time dependence of the products from the reaction $O + CH_4$. Signals at mass 15 (CH_3), 29 (CHO), and 32 (CD_2O) were observed with the argon lamp; $[CH_4]$ or $[CD_4] = 6 \times 10^{-6}$ mol l.$^{-1}$; $[O] = 1.5 \times 10^{-7}$ mol l.$^{-1}$; $[N_2] = 1.1 \times 10^{-4}$ mol l.$^{-1}$; flow velocity 5.6 m sec^{-1} in a 17.5-mm i.d. tube. The signal-to-noise ratio at mass 15 and 29 was approximately 10:1 for averaging times of 100 sec.

was balanced by its removal, reactions 2a and 2b. This

$$O + CH_4 \longrightarrow CH_3 + OH \qquad (1)$$

$$O + CH_3 \longrightarrow CH_2O + H \qquad (2a)$$

$$O + CH_3 \longrightarrow CHO + H_2 \qquad (2b)$$

reaction scheme requires that $[CH_3]_{ss}$ be proportional to $[CH_4]$ and independent of [O], as observed. A similar dependence of $[CHO]_{ss}$ on $[CH_4]$ and [O] was noted, which suggests that CHO radicals were destroyed by oxygen atoms. The CHO is not formed primarily by the reaction of formaldehyde with oxygen atoms, since this process would not produce a steady [CHO]. A small contribution to [CHO] from the $O + CH_2O$ reaction cannot be excluded due to the scatter in the mass 29 signal. Previous work[12] has suggested that the reaction of oxygen atoms with methyl radicals proceeds primarily *via* reaction 2a. The observation of CHO at the earliest times shows that the parallel channel, reaction 2b, cannot be neglected.

Work is in progress to calibrate the sensitivity of the instrument to CH_3 and other free radicals. An absolute determination of $[CH_3]_{ss}$, together with the known rate of reaction 1,[11] would establish the absolute rate constant for reaction 2, since at the steady state

$$k_2[CH_3]_{ss}[O] = k_1[CH_4][O]$$

Similar calculations can be performed for other steady-state free-radical concentrations, provided the reaction mechanism is understood.

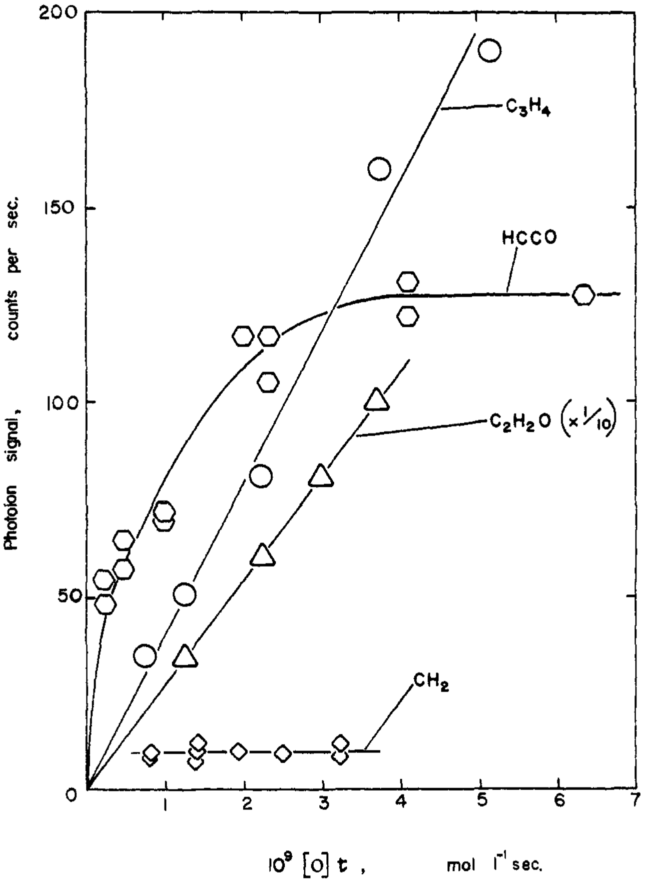

Figure 2. Products from the reaction $O + C_2H_2$ plotted against $[O]t$. The signal at mass 41 (HCCO) was observed at a constant reaction time, $t = 9 \times 10^{-3}$ sec, and $[C_2H_2] = 5.5 \times 10^{-7}$ mol l.$^{-1}$. Masses 42 (C_2H_2O), 40 (C_3H_4), and 14 (CH_2) were observed at a constant $[O] = 2.6 \times 10^{-7}$ mol l.$^{-1}$, and $[C_2H_2] = 2.4 \times 10^{-7}$ mol l.$^{-1}$. $[N_2] = 1.1 \times 10^{-4}$ mol l.$^{-1}$ for all experiments. Mass 14 was observed using an argon lamp and others were observed using a krypton lamp.

Investigation of the oxygen atom–acetylene reaction[9] established the presence of the free radicals CH_2, HCCO, C_3H_3, C_3H_2, and CHO, in addition to the stable products C_3H_4, C_2H_2O, and C_4H_2. The elusive CH_2 and the previously unobserved HCCO radical (eq 3) have been proposed as primary products in this

$$O + C_2H_2 \longrightarrow CH_2 + CO \qquad (3a)$$

$$O + C_2H_2 \longrightarrow HCCO + H \qquad (3b)$$

reaction.[13,14] Again steady-state concentrations were observed for both these radicals while the stable products grew linearly with reaction time (Figure 2). The CH_2 and HCCO are not fragmentation products of CH_2CO or other stable products because their concentrations possess a completely different time dependence. Figure 2 shows that it was possible to observe the approach of [HCCO] to its steady-state value by reducing [O] sufficiently. The rate constant for $O + HCCO$ can be determined directly from this rise to steady state.[9] Apparently the rate of $O + CH_2$ is considerably faster, since no corresponding approach of methylene to its steady-state concentration could be observed.

The radicals CH_3, CHO, and C_3H_7 were detected as products of the oxygen atom–ethylene reaction.

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Oxidation of ethane resulted in the formation of C_2H_5, C_2H_3, and C_3H_7 radicals.

It is suggested that the photoionization mass spectrometer will be extremely useful for studying gas-phase free-radical reactions. Any free radical with an ionization potential less than the argon resonance line energy (11.83 eV) and a steady-state concentration on the order of 10^{-10} mol/l. should be readily detectable in reacting gases at pressures of a few Torr. Improvements in detector design and pumping speed may improve this sensitivity by several orders of magnitude.

Acknowledgment. This work was sponsored by the Air Force Office of Scientific Research, Office of Aerospace Research, under Grant AFOSR-70-1872.

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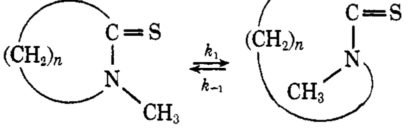
Molecular Structures of Medium- and Large-Membered *N*-Methylthiolactams and the Dynamics of Their Syn–Anti Interconversion

Sir:

A detailed conformational description of medium- (8–12) and large-membered ring compounds is potentially available from an approach which combines dynamic studies (nmr) and static molecular structure determination (X-ray).[1] We now report the molecular structures of the 9- and 13-membered *N*-methylthiolactams (I, n = 7 and 11), as well as activation parameters and thermodynamic equilibration data for the syn–anti interconversion (I ⇄ II) for the 12- and 13-membered ring systems.[2,3]



I, syn   II, anti

The 9-, 12-, and 13-membered *N*-methylthiolactams exist as crystalline solids; however, upon dissolution at room temperature in organic solvents the 12- and 13-membered systems display *N*-methyl doublet absorption in the nmr indicative of the equilibration process I ⇄ II. The nine-membered ring does not show this behavior due to the presence of only the syn form. Using the $W_{1/2}$ method for this $P_{\mathrm{I}} \neq P_{\mathrm{II}}$ system,[4a,b] the activation parameters listed in Table I were determined.

Table I. Activation Parameters for I ⇄ II Obtained by the $W_{1/2}$ Method and Direct Equilibration

Ring size	Solvent	E_a, kcal/mol	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	Method
12	$C_6H_5NO_2$	23.3	22.6	3.0	$W_{1/2}$
		22.8	22.1	6.2	$W_{1/2}$ + equil
13	$C_6H_5NO_2$	22.6	22.0	5.0	$W_{1/2}$
	$C_6H_5NO_2$ + $CDCl_3$	21.9	21.2	3.2	$W_{1/2}$ + equil
16	$C_6H_5NO_2$	22.4	21.7	5.0	$W_{1/2}$

With pure crystalline diastereomers in hand, E_a, $\Delta H^{\ddagger}$, and $\Delta S^{\ddagger}$ could also be obtained by direct equilibration.[5] To obtain these data (Table I) a crystalline sample of the 12- or 13-membered compounds was dissolved at −50°. Only one *N*-methyl peak occurred in the nmr at this temperature, and the relationship[6] $\ln([\mathrm{I}]_0 - [\mathrm{I}]_e)/([\mathrm{I}] - [\mathrm{I}]_e) = (k_1 + k_{-1})t$, where [I] = concentration of I at time t, $[\mathrm{I}]_0$ = concentration of I at t = 0, and $[\mathrm{I}]_e$ = concentration of I at equilibrium, was employed in the temperature range where equilibration took place (5–10°). Comparison of the results from the two methods reveals excellent internal agreement (Table I).

Furthermore, determination of the equilibrium constant $K = k_1/k_{-1}$ = II/I at various temperatures yielded the thermodynamic data listed in Table II. The syn form is enthalpically favored in both the 12- and 13-membered systems. As might be expected, the enthalpy difference is smaller in the larger ring.

Table II. Thermodynamic Parameters for I ⇄ II[a]

Ring size	$\Delta F_{273°}$, kcal/mol	ΔH, kcal/mol	ΔS, eu
12	2.60	2.38	−0.8
13	1.43	1.26	−0.6

[a] Obtained from a plot of log K *vs.* $1/T$.

The stereochemistry of both molecules was established by single-crystal X-ray analysis. The *syn*-*N*-methylthiocapryllactam crystallizes in the orthorhombic space group $Pna2_1$ with a = 16.621 (3), b = 8.729 (2), and c = 6.908 (2) Å. The lauryllactam crystallizes in the orthorhombic space group $P2_12_12_1$ with a = 12.266 (3), b = 17.193 (4), and c = 6.435 (2) Å. The structures were solved using the symbolic addition procedure for noncentrosymmetric crystals[7] and refined to final R factors of 0.043 for the capryllactam and 0.053 for the lauryllactam.

Figures 1 and 2 show the bond lengths and angles for the 9- and 13-membered *syn*-*N*-methylthiolactams, respectively. Table III presents the torsion angles.

The thioamido group in each case is nonplanar with a torsion angle of 12.8°. There are four antiperiplanar conformational units ($\omega \sim \pm 180°$) in *syn*-*N*-methylthiolauryllactam which would be expected in a ring of this size. Two antiperiplanar conformational units were found in 1,6-*trans*-diaminocyclodecane dihydrochloride (ten-membered ring),[8] four such units were

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