Oxirene Intermediate in the Reaction of Singlet Methylene with Carbon Monoxide[1]

Derek C. Montague and F. S. Rowland*

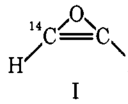
Contribution from the Department of Chemistry, University of California, Irvine, California 92664. *Received January 13, 1971*

Abstract: Singlet $^{14}CH_2$ from the photolysis of $^{14}CH_2CO$ reacts with CO with an isotopic carbon atom exchange to form ^{14}CO. At higher pressures, the intermediate can be collisionally stabilized. This intermediate is presumably oxirene, although there is no evidence for a stabilized adduct other than [^{14}C]ketene. While CO is capable of suppressing the reactions of $^3CH_2$ in mixed $^1CH_2/^3CH_2$ systems, the collision efficiency of O_2 toward $^3CH_2$ is 10^4 times greater than that of CO. The collision efficiency with CO of $^3CH_2$ is substantially less than is that of $^1CH_2$ with CO. A simple kinetic analysis permits an estimate of 0.10 for the ratio of rate constants for reaction of $^1(^{14}CH_2)$ with CO and with ketene. Approximately half of the $^{14}CH_2 + CO$ adducts are collisionally stabilized at 840 Torr of carbon monoxide.

The separation of the reactions of singlet methylene from those of triplet methylene in a particular photochemical system is dependent upon the discovery of suitable molecules which react preferentially with one form or the other of methylene, leaving a reasonably pure set of reactions attributable to the other spin state.[2] One very effective such additive is molecular O_2, which selectively prevents reaction of triplet methylene with hydrocarbon substrates even for O_2 levels in the PPM range.[3,4] Triplet methylene has also been shown to be *relatively* more reactive toward carbon monoxide in competition with ketene or 2-butene than is singlet methylene,[5] and a reasonably pure set of singlet methylene reactions can therefore be observed in excess carbon monoxide despite the presence of both singlet and triplet radicals in the original photolytically produced methylene.[6-10]

The utility of our earlier tracer studies[3,4,11-13] involving ketene photolysis has prompted us to study the reactions of $^{14}CH_2$ and CHT with carbon monoxide in competition with ketene and with *trans*-2-butene as substrates. Our experiments have confirmed many of the qualitative conclusions about the high *relative* efficiency of triplet methylene reaction with carbon monoxide, while demonstrating that the reaction of $^3CH_2$ with CO is nonetheless very inefficient, with a collision efficiency of $\leq 10^{-4}$.

In addition, we have also found that the reaction of singlet $^{14}CH_2$ with CO results in an isotopic carbon atom exchange, with the formation of ^{14}CO. The reaction has been shown to proceed through an intermediate capable of stabilization at high carbon monoxide pressure. The symmetrical nature of this reaction implies that the intermediate for the isotopic exchange has the oxirene structure (I). The oxirene intermediate has earlier been shown by ^{13}C-labeling techniques to exist in the two-stage process involving successive photolysis of α-diazo ketones or alkyl diazo acetates, and of the ketene products arising from the primary photolysis.[14-16] The oxirene has also been shown to be an intermediate in the photolysis of ketene itself, with an increasing amount of isotopic carbon atom exchange at very low pressures of ketene.[17]



I

Experimental Section

Carbon-14 labeled ketene, $^{14}CH_2CO$, was synthesized by the hot-tube vacuum pyrolysis of acetic-*2-*^{14}*C* anhydride (4.23 mCi/mmol, New England Nuclear Corp.).[18] More than 99.5% of the ^{14}C activity was originally contained in the methylene position of ketene. While photolysis of ketene has been shown to lead to scrambling of the ^{14}C labeling into the carbonyl position, this effect is negligible at the pressures used in these experiments.[17] Tritiated ketene, CHTCO, was prepared by the same method from acetic-*2-t* anhydride (50 mCi/mmol, New England Nuclear Corp.). The radioactive ketenes were purified by distillation *in vacuo* from −131 to −196°, and then thoroughly degassed before storage at −196°. *trans*-2-Butene (Phillips Research Grade) was used without further purification after degassing at −196°. Carbon monoxide (Matheson Co.) was purified by storage over activated charcoal, thereby reducing the oxygen concentration to less than 2 ppm. Tank oxygen was used without further purification.

Photolysis mixtures were made on a conventional mercury-free Pyrex vacuum system, employing grease-free stopcocks (G. Springham and Co., Viton A diaphragms). Pressure measurement was accomplished with a Wallace-Tiernan Model FA 145 mechanical dial manometer. Two separate cells were used with interchange-

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(1) This research was supported by Atomic Energy Commission Contract No. AT-(04-3)-34, Agreement No. 126.

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Table I. Radioactive Products from the 3130-Å Photolysis of Labeled Ketene in the Presence of *trans*-2-Butene, Carbon Monoxide, and Oxygen

	Composition, Torr				Product yields[a]						
								$[^{14}C]C_5H_{10}$ molecules			
Expt	$^{14}CH_2CO$	*trans*-2-Butene	CO	O_2	^{14}CO	$^{14}CO_2$[b]	$^{14}CH_2{=}CH_2$				
					$^{14}CH_2CO$, 3130 Å						
A	8.6	86	328	0	7.3	0.2	6.9	(25.7)	1.1	21.2	5.0
B	8.6	86	328	0.8	24.9	15.7	6.1	25.7	0.7	21.4	5.3
C	8.6	86	661	0	10.1	0.1	8.2	(25.7)	0.9	21.0	4.9
D	4.4	22	666	0	28.3	0.6	16.5	(25.7)	1.1	20.9	5.1
					CHTCO, 3130 Å						
	CHTCO				HT	$CH_2{=}CHT$	$CH_3CH{=}CHT$	C_5H_9T molecules			
	8.6	86	328	0	<0.05	10.0	<0.1	(25.7)	1.2	21.7	5.1
	8.6	86	328	0.1	3.9	9.1	0.33	(25.7)	1.1	21.9	5.0

[a] The product yields from O_2-scavenged $^{14}CH_2CO$ are given as per cent total observed volatile activity. All other runs have been normalized to 25.7% for the yield of *trans*-1,2-dimethylcyclopropane. The yields of other pentenes are: *cis*-2-pentene, <0.1; 3-methyl-1-butene, <0.1; 2-methyl-1-butene, <0.2. The yield of [^{14}C]propylene was <0.04. [b] Some propane-^{14}C may be included in this $^{14}CO_2$ total for O_2-free samples.

able results. Cell A was constructed of Vycor in cylindrical shape with a blown flat end window and a volume of 23.5 ml. Cell B was made from quartz, also cylindrical, with two parallel Suprasil end windows and a volume of 28.4 ml. Both cells were closed by Springham greaseless stopcocks.

Ketene was measured into the line from an acetone–solid CO_2 bath to inhibit the addition of diketene to the sample. Carbon monoxide was always added last to the photolysis mixture, and was introduced with the entire cell at −196°, except for a small dead volume of 0.06 ml.

All photolyses were carried out at room temperature 24 ± 1° using a super-pressure mercury arc (Osram HBO 200 W/2) in conjunction with a Bausch and Lomb high-intensity monochromator (Model No. 5, 74 Å/mm dispersion) to isolate the 3130-Å region of the spectrum with a half-band width of 40 Å. Constant light intensities were routinely employed during the photolyses, with frequent monitoring of the emission intensity from the lamp with an RCA 935 phototube. Photolyses usually lasted for 1–2 hr with approximately 2–4% decomposition of the ketene present.

After irradiation the reaction mixture was expanded into a previously evacuated gas-sampling injection loop prior to analysis on a standard radiogas chromatograph.[19] The sample was flushed from the loop with helium carrier gas through an anhydrous magnesium perchlorate stripper column to remove the unreacted ketene, thereby preventing the entry of radioactive contaminants into the analysis system. The components of the mixture were then separated with a dual column procedure, using a 50-ft $^1/_4$-in. column containing 35% by weight dimethylsulfolane on 30/60 mesh Chromosorb P-HMDS, together with a 20-ft $^3/_{16}$-in. column containing 18 wt % of a saturated solution of silver nitrate in ethylene glycol, also supported on 30/60 mesh Chromosorb P-HMDS. Complete resolution of all products was obtained by switching the silver nitrate column into and out of the gas stream at appropriate times. Radiogas chromatograms from similar separations are illustrated in detail elsewhere.[20]

Results and Discussion

Distribution of Radioactivity among Volatile Products. The experimental observation of DeGraff and Kistiakowsky[5] that $^3CH_2$ reactions can be suppressed by CO has been fully confirmed in our work. The data of Table I show the yields of the various volatile radioactive products found in several mixtures of $^{14}CH_2CO$–*trans*-2-butene–CO–O_2 and of CHTCO–*trans*-2-butene–CO–O_2. Since not all of the radioactive products following ketene photolysis appear in our radiogas chromatograms, the data have been arbitrarily normalized to a constant value for the yield of *trans*-1,2-dimethylcyclopropane.[21] In the O_2-scavenged $^{14}CH_2CO$ experiment, almost all of the products *do* appear in our radiogas chromatography, and the yield of *trans*-1,2-dimethylcyclopropane represents 25.7% of the total observed volatile activity; the other experiments are all expressed relative to this 25.7 as the standard.

It is readily apparent that the yields of the labeled C_5 products are essentially unaffected by the inclusion of small amounts of O_2 during the photolysis. Since these C_5 yields consist almost entirely of the three compounds formed by stereospecific insertion into $>C{=}C<$ and C—H bonds of the substrate *trans*-2-butene, the reactions leading to C_5 products are attributed to singlet methylene. In agreement with earlier observations,[5,9] the reactions of $^3CH_2$ with *trans*-2-butene are fully suppressed by an excess of CO. The mechanism of suppression actually changes with the addition of O_2 because it is able to compete successfully with the excess CO for $^3CH_2$, but *trans*-2-butene is ineffective in competing with either O_2 or excess CO in the absence of O_2 for the $^3CH_2$ present in the system. In the absence of O_2, the yield of *cis*-1,2-dimethylcyclopropane is about 0.4 higher than found with O_2 scavenger present. If this incremental yield is attributed entirely—and this may be an overestimate—to the reactions of triplet CH_2, then the total triplet reaction yield for methylene reacting with *trans*-2-butene is estimated to be <5%, even without the addition of O_2.

Examination of the yields of the low-molecular-weight products, however, reveals several interesting facets of information. (a) The yield of $^{14}CH_2{=}CH_2$ is substantially less than that of $CH_2{=}CHT$ under otherwise comparable conditions. (b) ^{14}CO is formed in O_2-free experiments with $^{14}CH_2CO$. (c) The yields of ^{14}CO and $^{14}CO_2$ are increased by about 17.6% and 15.5%, respectively, with the addition of a small quantity of O_2 to $^{14}CH_2CO$. (d) Yields of HT and $CH_3CH{=}CHT$ appear with the introduction of O_2 into CHTCO experiments.

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(21) This normalization is roughly the equivalent in O_2-free runs to normalization to a total observed volatile yield of 60–70%, in reasonable agreement with the estimated fraction of $^1CH_2$ formed in 3130-Å photolysis of ketene. The actual yield of $^3CH_2$ is the sum of that originally formed as $^3CH_2$ plus that collisionally converted from $^1CH_2$—the latter being dependent on the number and charge density of other molecules present.

Table II. Formation of $^{14}CH_2{=}CH_2$ and ^{14}CO by Photolysis of $^{14}CH_2CO$ with CO

Mole ratio CO:ketene	Total pressure,[a] Torr	Obsd ratio $^{14}CH_2{=}CH_2:^{14}CO$	Obsd counts as ^{14}CO ($\times10^3$)	Est rel yield[b]	Oxirene correction[c]	Corrected ratio $^{14}CH_2{=}CH_2:^{14}CO$
15.6	72.1	3.39	30.9	27.0	0.040	3.96
36.3	162	1.75	28.9	26.8	0.038	1.98
54.1	244	1.29	26.0	24.8	0.035	1.44
76.2	341	0.95	23.2	22.6	0.032	1.07
99.6	448	0.79	24.8	24.9	0.030	0.89
153	669	0.59	17.8	18.8	0.026	0.66
175	765	0.52	18.2	19.7	0.024	0.58
198	878	0.44	17.4	19.3	0.022	0.50

[a] Pressure of $^{14}CH_2CO$ is approximately 4.4 Torr in all experiments. Only minor amounts of other radioactive products were observed. [b] Observed counts of ^{14}CO minus corrections for oxirene intermediate in photolysis of ketene and for $CH_2{}^{14}CO$ impurity in $^{14}CH_2CO$, then increased to correct for nonunit quantum yield in $^{14}CH_2CO$ decomposition, based upon $\Phi = 0.95$ for 200 Torr of N_2 (ref 5), with N_2 and CO assumed equal in efficiency. [c] Estimated fractional yield of ^{14}CO from photolytically induced oxirene rearrangement of ketene (ref 17).

The difference in yield between $^{14}CH_2{=}CH_2$ and $CH_2{=}CHT$ is essentially an isotope effect in the tritiated system.[22] Similar measurements with *trans*-2-butene in the absence of CO show a yield ratio under comparable conditions of $(^{14}CH_2{=}CH_2):(CH_2{=}CHT) = 0.71 \pm 0.01$[22] only slightly higher than the 0.68 ± 0.01 observed for the two examples in Table I. This effect is thus not primarily the result of having excess CO in the system, although the minor remaining difference will be discussed later.

The last two observations are readily explained as the consequences of triplet methylene reactions with O_2, for which labeling experiments with $^{14}CH_2$ have shown the formation of approximately equal amounts of ^{14}CO and $^{14}CO_2$ by reactions 1 and 2.[3] The comparable reactions

$$^3(^{14}CH_2) + O_2 \longrightarrow {}^{14}CO_2 + H_2 \qquad (1)$$

$$^3(^{14}CH_2) + O_2 \longrightarrow {}^{14}CO + H_2O \qquad (2)$$

$$^3CHT + O_2 \longrightarrow CO_2 + HT \qquad (3)$$

$$^3CHT + O_2 \longrightarrow CO + HTO^* \longrightarrow T^* + OH \text{ or } H^* + OT \qquad (4)$$

3 and 4 with CHT produce the HT observed in O_2-scavenged CHTCO, as well as HTO, OT, and T*. The subsequent reaction of the energetic T* with *trans*-2-butene leads to $CH_3CH{=}CHT$ by reaction 5; the *sec*-butyl radical formed in (5) does not decompose at these pressures unless the reaction is initiated by a tritium atom with more than thermal kinetic energy.[23] The absence of ^{14}C-labeled propylene in comparable experiments with $^{14}CH_2CO$ shows clearly that the tritium atom in $CH_3CH{=}CHT$ is no longer a methylene tracer, but is actually tracing only the reactions of the hydrogen atoms originating from methylene.[24] Since the incremental yield of ^{14}CO plus $^{14}CO_2$ (approximately 33%) is essentially the total anticipated triplet component in this system and is composed of approximately equal amounts of both products, we conclude that >95% of the $^3(^{14}CH_2)$ reacts with O_2 rather than with CO despite the 410-fold initial excess of the latter.

$$T^* + CH_3CH{=}CHCH_3 \longrightarrow CH_3CHTCHCH_3^* \longrightarrow CH_3CH{=}CHT + CH_3 \qquad (5)$$

More stringent tests of the precise magnitude of the relative reactive superiority of O_2 to CO for triplet methylene pose some experimental problems, since the O_2 is removed as it scavenges. Thus, photolysis of a mixture containing $^{14}CH_2CO$–*trans*-2-butene–CO–O_2 in the ratio 8.6:86:328:0.008 would result in the removal of *all* of the O_2 with about 0.2% photolysis of the initial ketene. Scavenging was incomplete in the run (Table I) with 0.1 Torr of O_2 plus CHTCO because of exhaustion of the scavenger near the end of the run. Similarly, the small yield of $^{14}CO_2$ from supposedly "O_2-free $^{14}CH_2CO$ experiments" are indicative of small traces (<10 ppm) of adventitious O_2 at the beginning of such experiments.

The interesting new observation from Table I is the formation of an appreciable ^{14}CO yield in the absence of O_2. While some ^{14}CO is anticipated from the photochemically induced oxirene rearrangement of ketene,[17] the per cent ^{14}CO found in experiments at 600 Torr in the absence of CO is only about 3% of the total radioactivity, far below that corresponding to the highest value, 28.3, listed in Table I. Additional experiments with $^{14}CH_2CO$ and inactive CO showed conclusively (Table II) that this extra ^{14}CO is formed by reaction of $^{14}CH_2$ with CO, with the ^{14}CO yield eventually becoming more than double that of $^{14}CH_2{=}CH_2$. Since the formation of this ^{14}CO is independent of the addition of O_2—and the accompanying diversion of $^3(^{14}CH_2)$ reactions from CO to O_2—the source must lie in some reaction of $^1(^{14}CH_2)$ with CO. The conversion of $^{14}CH_2$ to ^{14}CO must then proceed through some intermediate with the oxirene structure (I) which permits the interchange of ^{14}C with the nonradioactive carbon atoms from CO.

Since a substantial contribution to the formation of labeled ethylene comes from the attack of labeled methylene upon unlabeled ketene (6), it is clear that loss of ^{14}C through the oxirene intermediate can lead to a reduction in the anticipated yield of $^{14}CH_2{=}CH_2$. The other contributor to labeled ethylene formation—the attack of unlabeled methylene upon labeled ketene, as in (7)—is unaffected by the existence of the oxirene intermediate, providing that the intermediate decomposes and is not converted to ketene by collisional stabiliza-

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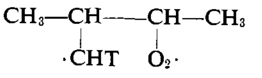
(24) It should be noted that the identification of $CH_3CH{=}CHT$ as a product from CHT reactions with O_2-scavenged $CH_3CH{=}CHCH_3$ was erroneously accepted by C. McKnight and F. S. Rowland, *ibid.*, **88**, 3179 (1966), as evidence for the decomposition of the intermediate



$$\begin{array}{cccc} CH_3{-}CH & \text{——} & CH{-}CH_3 \\ | & & | \\ \cdot CHT & & O_2\cdot \end{array}$$

previously postulated by R. W. Carr, Jr., and G. B. Kistiakowsky, *J. Phys. Chem.*, 70, 118 (1966), in such systems. Such an intermediate does not exist because of the prior interception of CHT radicals by O_2; the absence of decomposition from a C_5–O_2 intermediate is shown by the absence of ^{14}C-labeled propylene in $^{14}CH_2CO$-*trans*-2-butene-O_2 experiments (see footnote *a*, Table I).

tion. In the absence of an oxirene-like intermediate and/or isotope effects in the reactions, the contributions from (6) and (7) are equal.

$$^{1}(^{14}CH_2) + CH_2CO \longrightarrow {}^{14}CH_2{=}CH_2 + CO \quad (6)$$

$$^{1}CH_2 + {}^{14}CH_2CO \longrightarrow {}^{14}CH_2{=}CH_2 + CO \quad (7)$$

An additional qualitative conclusion can be drawn from Table II; *i.e.*, although an increase in the CO:ketene ratio reduces the $^{14}CH_2{=}CH_2$:^{14}CO ratio, it does not do so with an increase in the absolute ^{14}CO yield, for the actual observed ^{14}CO yield decreases by almost a factor of 2 in the data of Table II. A small part of this decrease in ^{14}CO yield can be attributed to pressure-dependent suppression of the initial photolysis of ketene by the increased CO pressure. An approximate correction for the initial quantum yield of $^{14}CH_2CO$ has been applied to obtain the data in the fifth column of Table II, using the quantum yield measurements of DeGraff and Kistiakowsky.[25] The more important factor, however, in the diminishing ^{14}CO yield is the suppression of the decomposition of the oxirene intermediate by higher pressure. The net result of the addition of CO to a constant pressure of $^{14}CH_2CO$ is the prevention of $^{14}CH_2{=}CH_2$ formation by diversion of $^{14}CH_2$ into reaction with CO, chiefly with the formation of a stabilized $^{14}CCH_2O$ molecule.

Relative Reaction Efficiencies of $^{1}CH_2$ and $^{3}CH_2$. DeGraff and Kistiakowsky interpreted their earlier experiments on the photolysis of ketene in the presence of CO in terms of competitions between CO and ketene for both $^{1}CH_2$ and $^{3}CH_2$, as in eq 8–11.[5] Their results

$$^{1}CH_2 + CH_2CO \longrightarrow \text{products} \quad (8)$$

$$^{1}CH_2 + CO \longrightarrow CH_2CO \quad (9)$$

$$^{3}CH_2 + CH_2CO \longrightarrow \text{products} \quad (10)$$

$$^{3}CH_2 + CO \longrightarrow CH_2CO \quad (11)$$

gave relative reaction rates of $k_{11}/k_{10} = 3.6$ at 3160 Å, and $k_9/k_8 = 0.14 \pm 0.02$. In the absence of any convincing evidence to the contrary, they made the provisional assumption that $k_8 = k_{10}$ and therefore that $k_{11} \cong 25k_9$, and suggested a possible electronic explanation for this apparently high relative reactivity of $^{3}CH_2$ *vs.* $^{1}CH_2$.[5] Other experiments have also been interpreted as furnishing supporting evidence for this high reactivity of CO toward $^{3}CH_2$.[7] However, subsequent flash photolysis experiments have provided ample evidence for the generally high collision efficiencies of singlet methylene reactions, as well as for the relative nonreactivity of triplet methylene.[26] The observation of radical–radical reactions involving $^{3}CH_2$ in ordinary photolysis systems implies very low collision efficiencies toward reaction with the stable molecules in these systems.[4,27]

The data of Table I show the interception by O_2 of almost all of the $^{3}(^{14}CH_2)$ which would otherwise have reacted with CO. Assuming that at most a few per cent of the $^{3}(^{14}CH_2)$ might still be reacting with CO, and allowing for the 410-fold initial ratio of CO/O_2, the reaction of $^{3}CH_2$ with O_2 can be estimated to have a collision efficiency $\geqslant 10^4$ times greater than that with CO. Another estimate of the upper limit on the collision efficiency of reaction 10 can be placed by the observation of $^{3}CH_2$–$^{3}CH_2$ reactions in systems with 1% ketene present, from which the relative efficiency of (10) cannot be more than 10^{-6} times that of the reaction of two triplets with each other. Since suppression of $^{3}CH_2$ reactions requires *excess* amounts of CO, the collision efficiency of $^{3}CH_2$ with CO must be $\lesssim 10^{-5}$. We therefore do not describe CO as a "scavenger" for $^{3}CH_2$—the reaction is very inefficient, and suppression of other $^{3}CH_2$ reactions is not achieved with minor amounts of CO, but only with CO as the major component. The observed efficacy of CO in removing $^{3}CH_2$ from reaction systems therefore results chiefly from the extremely low collision efficiencies of the other $^{3}CH_2$ reactions with which it must compete.

Since the reactions of $^{1}CH_2$ with a variety of substrates with which CO is reasonably competitive show collision efficiencies >0.01,[26] the relative collision efficiency of $k_{11}/k_9 \ll 0.01$. The inferred high relative reactivity of $^{3}CH_2$ *vs.* $^{1}CH_2$ in reactions with CO is thus not supported by the experimental data, depending as it did on the faulty assumption that $k_8 \cong k_{10}$.

Simple Kinetic Treatment. The overall kinetic description of these systems can be quite complicated, especially when the possibility must be included that the rates of any or all of the $^{1}CH_2$ reactions may be dependent upon the vibrational excitation energy carried by the methylene at the time of reaction.[2] Nevertheless, a simplified kinetic scheme can be used to provide semiquantitative agreement with the data of Table II. The scheme includes the competitive reactions of $^{1}(^{14}CH_2)$ with CH_2CO and CO (reactions 6 and 12)—assumed independent of the excitation of the singlet—plus the further competition between stabilization and decomposition of the excited $^{14}CCH_2O$ intermediate, as in (13) and (14). All triplet methylenes are assumed to be removed permanently by reaction 11. If the methylene products of (14) are assumed to be in the singlet state and capable

$$^{1}(^{14}CH_2) + CO \longrightarrow {}^{14}CCH_2O^{*} \quad (12)$$

$$^{14}CCH_2O^{*} + M \longrightarrow {}^{14}CCH_2O + M \quad (13)$$

$$^{14}CCH_2O^{*} \longrightarrow \begin{cases} {}^{14}CH_2 + CO & (14a) \\ CH_2 + {}^{14}CO & (14b) \end{cases}$$

of undergoing (6) or (12), then steady-state expressions can be written for $^{1}(^{14}CH_2)$, $^{1}CH_2$, $^{14}CCH_2O^{*}$, and $C_2H_2O^{*}$. Neglecting any isotopic differences in the rates of reactions 6–14, the relative rates of formation of $^{14}CH_2{=}CH_2$ [from (6) plus (7)] and ^{14}CO [from (14b)] are then given by eq 15. In (15), Ke is the ketene concentration, k_{14} is the sum of decomposition by both (14a) and (14b), and M is the appropriately weighted sum of the stabilizing efficiencies of CO and ketene.

$$\left[\frac{^{14}CH_2{=}CH_2}{^{14}CO}\right] = \frac{4k_6(\text{Ke})}{k_{12}(\text{CO})}\left(1 + \frac{k_{13}M}{2k_{14}}\right) + \frac{1}{1 + \dfrac{k_{12}(\text{CO})}{k_6(\text{Ke})}\left(1 - \dfrac{1}{\left(1 + \dfrac{k_{13}M}{2k_{14}}\right)}\right)} \quad (15)$$

Despite the relative complexity of this equation, it has only two disposable parameters—the rate constant

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[25] DeGraff and Kistiakowsky showed that N_2 is an inefficient quencher relative to ketene itself for excited ketene, and assumed that the quenching efficiency of CO would be equivalent to that of the isoelectronic N_2.[5] Their measured 5% diminution in quantum yield for 200 Torr of N_2 is the basis for the corrections calculated in Table II.

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[27] H. M. Frey and R. Walsh, *J. Chem. Soc. A*, 2115 (1970).

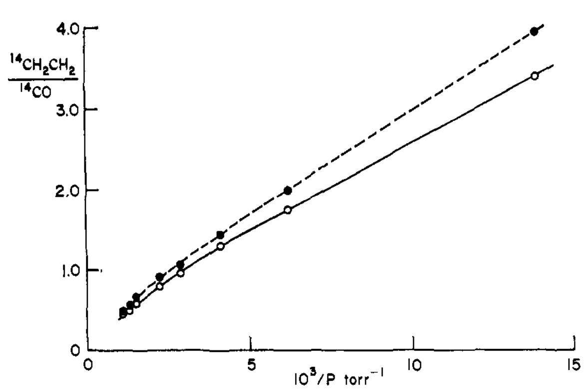

Figure 1. Calculated and experimental ratios of $^{14}CH_2{=}CH_2$/^{14}CO *vs.* (pressure)$^{-1}$ with increasing CO pressure at constant ketene pressure (4.4 Torr): ○, observed experimental ratios; ● experimental ratios corrected for ^{14}CO from oxirene in photodecomposition of ketene, and for $CH_2{}^{14}CO$ in $^{14}CH_2CO$; —, calculated with $k_{12}/k_6 = 0.11$ and $k_{13}/k_{14} = 1.4 \times 10^{-3}$ Torr^{-1}; ---, calculated with $k_{12}/k_6 = 0.10$ and $k_{13}/k_{14} = 1.2 \times 10^{-3}$ Torr^{-1}.

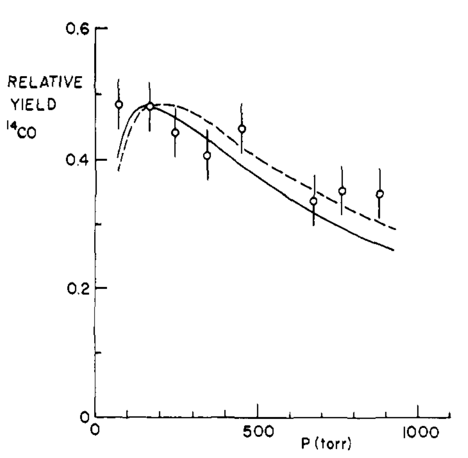

Figure 2. Calculated and experimental relative yields of ^{14}CO *vs.* increased CO pressure at constant ketene pressure (4.4 Torr): ○, experimental relative yields (Table II); —, calculated with $k_{12}/k_6 = 0.11$ and $k_{13}/k_{14} = 1.4 \times 10^{-3}$ Torr^{-1}; ---, calculated with $k_{12}/k_6 = 0.10$ and $k_{13}/k_{14} = 1.2 \times 10^{-3}$ Torr^{-1}.

ratios k_{12}/k_6 and k_{13}/k_{14}. An excellent fit to the measured ($^{14}CH_2CH_2$):(^{14}CO) ratios is obtained with the values $k_{12}/k_6 = 0.11$ and $k_{13}/k_{14} = 1.4 \times 10^{-3}$ Torr^{-1}, as shown in Figure 1. In these calculations, M has simply been chosen as the sum of the pressures of all gaseous components.

The absolute yields of the products, per molecule of $^{14}CH_2CO$ photolyzed, can also be written from these steady-state expressions, as given in (16) for the formation of ^{14}CO. The estimated relative yields of Table II are compared with these absolute yields from eq 16 in Figure 2. (Since actual quantum yields for ketene photolysis are difficult to measure in excess CO, the relative yields have been arbitrarily normalized in absolute magnitude.) The calculated curve is in agreement with the experimentally observed diminution of ^{14}CO activity at higher pressures, but also suggests a maximum at lower pressures not found in the experiments. While our relative yields are not very accurately known, the absence of this maximum is probably an experimental fact.

$$\Psi(^{14}CO) = \left[1 + \frac{k_{13}M}{k_{14}} + \frac{2k_6(\mathrm{Ke})}{k_{12}(\mathrm{CO})}\left(1 + \frac{k_{13}M}{k_{14}}\right)\right]^{-1} \tag{16}$$

Variation in the relative efficiency of ketene and CO as the colliding body in reaction 13 has little effect on the data fit, since most deexcitations occur with the great excess of CO in any case. For example, even with the grossly exaggerated assumption that ketene is 10 times as efficient as CO in stabilizing (13), the rate constant ratios are $k_{12}/k_6 = 0.12$ and $k_{13}/k_{14} = 1.5 \times 10^{-3}$ Torr^{-1} for the fit to the data. These changes are so minor that these possible variations in collision efficiency are ignored in the sections below. If the $C_2H_2O^*$ molecules are efficiently deexcited by collisions with CO, the values of k_{13}/k_{14} imply that the oxirene intermediate has an average decomposition rate of about 3×10^9 sec^{-1}.

Corrections for Oxirene in Photodecomposition of Ketene. The directly measured $^{14}CH_2{=}CH_2$:^{14}CO ratios of Table II include some ^{14}CO from the photochemical formation of oxirene directly from ketene,[17] and a correction should be made for the presence of ^{14}CO from this source. There is, however, some uncertainty in the precise magnitude of the correction to be made under our conditions. We have made our best current estimate for this correction by the procedure described in the Appendix. The fractional oxirene correction, plus a minor correction for the presence of $CH_2{}^{14}CO$ in the original ketene, is given in the sixth column of Table I, and the corrected ratios of $^{14}CH_2{=}CH_2$:^{14}CO are given in the last column of that table.

With the corrected data, application of the steady-state kinetic scheme gives new ratios of rate constants ($k_{12}/k_6 = 0.10$ and $k_{13}/k_{14} = 1.2 \times 10^{-3}$ Torr^{-1}), as shown by the dotted line of Figure 1. The new predicted fractional yields are also shown by the dotted line in Figure 2. While this correction procedure is somewhat arbitrary in view of our lack of knowledge of the effects of CO or other molecules upon the photochemical rearrangement of ketene, the resulting data of Figures 1 and 2 lead only to minor quantitative changes in the conclusions obtained from the data without correction for other sources of ^{14}CO. The experimental estimated relative yield data plotted on Figure 2 are taken from the fifth column of Table II. These relative yields have then been arbitrarily normalized to give approximate agreement with the dotted line calculation from eq 16.

Our value of 0.20 for k_{12}/k_6 is in reasonable agreement with the earlier value of 0.14 ± 0.02 for the comparable k_9/k_8.[5] However, DeGraff and Kistiakowsky assumed in their analysis that the excited CH_2CO^* molecule was always stabilized, *i.e.*, $k_{14} = 0$. At their experimental pressures (mostly 10–250 Torr), stabilization of the $^{14}CCH_2O$ intermediate is a minor factor with our value of k_{13}/k_{14}, in direct contrast to their assumption of complete stabilization. Our results indicate that 50% or more of the $^{14}CCH_2O$ complexes are stabilized only at pressures of 840 Torr or above.

Qualitative Mechanistic Modifications. The assumption that the methylenes formed from (14) are always equivalent in reactivity to the initial methylenes is quite doubtful, since a fraction may very well be $^3CH_2$, while the average vibrational excitation energy of $^1CH_2$ formed by (14) is not likely to be as large as that formed by the direct photolysis of ketene at 3130 Å.[2] If reaction 14 is assumed to give a specified mixture of $^1CH_2$ and $^3CH_2$, satisfactory fits similar to Figure 1 can

Table III. Predicted and Measured Experimental Yields from $^{14}CH_2CO$–*trans*-2-Butene–CO Mixtures

	Experiment (Table I) A		C		D	
	Calcd	Obsd	Calcd	Obsd	Calcd	Obsd
Product						
trans-1,2-DMC	(25.7)	(25.7)	(25.7)	(25.7)	(25.7)	(25.7)
Other C_5	(27.3)	27.3	(27.3)	26.8	(27.3)	27.1
$^{14}CH_2{=}CH_2$ from (6)	3.31		3.31		6.65	
$^{14}CH_2{=}CH_2$ from (7)	3.54		3.61		8.34	
Total $^{14}CH_2{=}CH_2$	6.85	6.9	6.92	8.2	15.0	16.5
^{14}CO, uncorr		7.3		10.1		28.3
^{14}CO, corr	4.0	4.1[a]	6.45	6.9[a]	26.4	22.7[a]
Stabilized $^{14}CCH_2O$	4.1		11.6		43.5	

[a] Corrected for photoinduced oxirene decomposition of ketene, and for $CH_2{}^{14}CO$ impurity. For example, in D, estimate for 692 Torr that 0.025 of the photolyses lead to ^{14}CO by oxirene–ketene, and 0.005 from $CH_2{}^{14}CO$. For the $^{14}CH_2$ actually formed by the photolysis, the calculated distribution is C_5, 0.409; stabilized $^{14}CCH_2O$, 0.336; ^{14}CO, 0.204; $^{14}CH_2CH_2$, 0.051 (plus $^{14}CH_2CH_2$, 0.065 from $CH_2 + {}^{14}CH_2CO$). The correction is then $(0.030)(25.7 + 27.3)/(0.7)(0.409) = 5.6$, assuming that the fraction of methylene formed as singlet is 0.7.

still be obtained for singlet fractions as low as one-third. The relative yield data of Figure 2 are not quite as well simulated if a major fraction of $^3CH_2$ is assumed from reaction 14, tending to move the maximum to higher pressures with a lesser slope at the highest pressures. The rate constant ratios for the best fit to the data change only slowly with changes in the assumption of the fraction of singlet methylene from (14), and do not affect qualitative conclusions or arguments.

Two other implicit assumptions are less probable sources of serious error. First, while $^1CH_2 \rightarrow {}^3CH_2$ conversion in collision with CO is a possible alternate outcome to reaction 12,[28] its estimated collision efficiency suggests that it is less probable than (12) by a factor of 10–100,[5,9] and therefore only a small perturbation in the kinetic calculations. Second, the reaction of $^1CH_2$ with ketene seems to lead to ethylene in a very high percentage of reactions, and alternate outcomes to reaction 6 can also be neglected.

Competition with *trans*-2-Butene. The data of Table I can be compared with the expectations from the mechanism outlined above by the inclusion of reaction 17 with *trans*-2-butene. Assuming that $k_{17}/k_6 = 1.6$, the

$$^1(^{14}CH_2) + trans\text{-}CH_3CH{=}CHCH_3 \longrightarrow \text{stereospecific products} \quad (17)$$

relative yields are calculated as given in Table III, and are in reasonable agreement with the data. Again, the ^{14}CO yields have been corrected for the formation of ^{14}CO from photolysis of impurity $CH_2{}^{14}CO$ and from the photolytically induced oxirene rearrangement of ketene. The calculated $^{14}CH_2{=}CH_2$ yield has been divided into the components arising separately from reactions 6 and 7 to illustrate their nonequivalence following some ^{14}C loss to ^{14}CO through the oxirene intermediate. The calculated loss of $^{14}CH_2$ to stabilized intermediate is also shown in Table III, although no experimental data are available for comparison.

The data trends are clearly consistent with the expectation from the mechanism: $^{14}CH_2{=}CH_2$ increases relative to [^{14}C]*trans*-1,2-dimethylcyclopropane with increased CO pressure, since $^{14}CH_2{=}CH_2$ can be formed by both (6) and (7) while the C_5 adduct can be formed only by reaction of $^{14}CH_2$, as in (17). Since an increased participation of the oxirene decreases the importance of both $^{14}CH_2$ reactions relative to that of CH_2 on $^{14}CH_2CO$, the ratio of $^{14}CH_2{=}CH_2$ to this shrinking standard must rise. Similarly, an increased CO:ketene ratio results in lower $^{14}CH_2{=}CH_2$:^{14}CO ratios, just as also found in Table II. The rate constant ratio k_{17}/k_6 of 1.6 ± 0.2 is in agreement with the earlier value of 1.4 ± 0.3,[5] within the wide margins for error.

In the absence of isotope effects on the rates of reaction, the measured yield of $CH_2{=}CHT$ would be expected to be higher than that of $^{14}CH_2{=}CH_2$ in comparable experiments because the oxirene intermediate would not partially deplete the tritium label of methylene as it does the ^{14}C label. In experiment C of Table III, for instance, an undepleted label in ethylene should be higher by $(2 \times 3.61)/(3.31 + 3.61)$ or $(7.22)/(6.91)$, than the partially depleted ^{14}C label. Such an effect in relative yields of $^{14}CH_2{=}CH_2$ and $CH_2{=}CHT$ under comparable conditions is overshadowed by the isotope effects in the tritium system.[22] However, the small difference between the $^{14}CH_2{=}CH_2$:$CH_2{=}CHT$ ratios of Table I (0.68 ± 0.01) and that found in CO-free systems (0.71 ± 0.01)[22] is approximately of the correct magnitude for the ^{14}C depletion estimated for the oxirene intermediate in the *trans*-2-butene systems of Table III.

Vibrational Excitation of Methylene. One additional parameter might also be varied in a more complex kinetic treatment—the effect of excitation energy of the singlet methylene.[2] It seems quite possible that the value of k_{12}/k_6 varies with the excitation energy of the reacting $^1(^{14}CH_2)$, and almost certain that the decomposition rate, k_{14}, of excited $^{14}CCH_2O$ will increase steadily as more vibrational energy of $^1(^{14}CH_2)$ is added to the exothermicity of the addition reaction itself. A more detailed kinetic scheme would then allow for variation in k_{14} and in k_{12}/k_6 with the excitation energy of the singlet methylene. The slight discrepancy in shape of calculated *vs.* experimental curve in Figure 2 may well arise from our failure to provide for these variations in our kinetic scheme. However, the available data do not warrant any increase in the number of disposable parameters used for a kinetic fit. Further investigation of the precise kinetic description of this isotopic carbon atom exchange process will require a much more elaborate series of experiments with irradiations at various wavelengths, measurement of the relative stabilization efficiencies of different molecules in reaction 13, use of several substrate molecules in competition, etc.

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Oxirene. The existence of the oxirene intermediate is well established in several other experiments, and its occurrence here is quite consistent with the chemistry involved in these other systems.[14–17] The re-formation of ketene by reaction of CH_2 with CO was established many years ago,[29,30] and the eventual identity of the C_2H_2O molecule created by reactions 11 or 13 is almost certainly ketene. There is no evidence that the addition product of $^3CH_2$ with CO ever attains the oxirene structure; if the oxirene is formed, its lifetime must be sufficiently long for complete stabilization under our conditions, since no ^{14}CO of $^3(^{14}CH_2)$ origin has yet been found. Failure to form the oxirene structure in $^3CH_2$ + CO reactions could be equally well explained in our experiments by the lower total exothermicity available with the ground state $^3CH_2$ reactant, or to spin differences in the reaction itself.

There exists the possibility that the stabilizing collisions of (13) result in the formation of stabilized oxirene itself—however, no evidence for its stable existence has yet been found, and isomerization to ketene must be a relatively easy process.[14–17]

Acknowledgment. The comments of Mr. Robert L. Russell are gratefully acknowledged.

Appendix. Correction of Data for ^{14}CO Formed by Photochemically Induced Oxirene Rearrangement of Ketene

The pressure-dependent fractional yield for the formation of ^{14}CO per molecule of $^{14}CH_2CO$ actually decomposed in the direct photolysis of $^{14}CH_2CO$ has been estimated from the data of ref 17. This correction ranges from 0.040 at 72 Torr to 0.022 at 880 Torr; a constant 0.005 has been added to correct for 0.5% $CH_2{}^{14}CO$ present as an isotopic positional impurity in the original $^{14}CH_2CO$.[17] Approximately 30%[2] of the photodecomposed molecules at 3130 Å produce $^3(^{14}CH_2)$, which is removed by reaction with CO and does not appear in the measured products. The formation of ^{14}CO from the initial decomposition of $^{14}CH_2CO$ has been assumed to be equal to the fractional yield calculated by eq 16 at that pressure (Figure 2), multiplied by 0.70 for the fraction giving $^1(^{14}CH_2)$ in the photodecomposition.

For example, at 162 Torr, the first calculated fractional yield is (0.483)(0.70) = 0.338 and the oxirene-plus-$CH_2{}^{14}CO$ correction is 0.038 + 0.005 = 0.043. The observed $^{14}CH_2{=}CH_2:{}^{14}CO$ ratio is then multiplied by (0.338 ± 0.043)/(0.338) to obtain the $^{14}CH_2{=}CH_2:{}^{14}CO$ ratio applicable to eq 6 and 12–14.

A new set of rate constant ratios was calculated to fit this corrected set of experimental data, and then a new set of fractional yields *vs.* pressure was calculated from these rate constant ratios. Recalculation of the applicable corrections with this revised set of fractional yields led to another revised set of corrected experimental $^{14}CH_2{=}CH_2:{}^{14}CO$ ratios, etc.; the process converged rapidly, with the final results shown in Table II and Figures 1 and 2.

The experimental relative yields have been corrected by subtracting the ^{14}CO of other origin from the observed ^{14}CO counts (same factors as above), and then applying the quantum yield correction estimated from the measurements of DeGraff and Kistiakowsky.

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