Lawrence Berkeley National Laboratory

Recent Work

Title

SCAVENGER EFFECTS IN THE RECOIL TRITIUM REACTIONS OF CYCLOHEXENE

Permalink

<https://escholarship.org/uc/item/2d36f09v>

Author

Fee, Darrell C.

Publication Date

1972-05-01

SCAVENGER EFFECTS IN THE RECOIL TRITIUM
REACTIONS OF CYCLOHEXENE

Darrell C. Fee, and Samuel S. Markowitz

May 1972

AEC Contract No. W-7405-eng-48

For Reference

Not to be taken from this room

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

SCAVENGER EFFECTS IN THE RECOIL TRITIUM REACTIONS OF CYCLOHEXENE*

Darrell C. Fee and Samuel S. Markowitz

Department of Chemistry and
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

May 1972

ABSTRACT

The comparative efficiency of H_2S , butadiene- d_6 , O_2 and SO_2 as radical scavengers has been determined in the T + cyclohexene gas phase system. The T was produced by recoil in the $^3\text{He}(\text{n},\text{p})\text{T}$ reaction. Direct tritium substitution on cyclohexene yields cyclohexene-t which may undergo unimolecular decomposition to produce butadiene-t. In unscavenged samples butadiene-t is selectively depleted by reactions with H atoms produced by radiolysis. Neither SO_2 nor H_2S is sufficiently reactive with H atoms to protect butadiene-t from such depletion. The "hot" butadiene-t yield can only be determined by means of O_2 or butadiene- d_6 scavenging. All products except butadiene-t exhibit normal behavior with O_2 , SO_2 or H_2S scavenging.

Many recoil tritium experiments have used scavengers to remove thermalized tritium atoms and radical intermediates from the system before such species can yield products which might be confused with high-energy tritium reactions [1]. The yield of products formed solely by high energy (hot) reactions will remain unchanged over a wide range of scavenger concentrations. The yield of products formed by both thermal and hot processes will decrease rapidly with the addition of scavenger until a plateau is reached where the yield becomes relatively insensitive to scavenger concentration. In this region all thermal reactions, except with the scavenger, have presumably been suppressed and the yield is due entirely to hot reactions [2].

The comparative efficiency of sulfur dioxide and oxygen as radical scavengers has recently been determined in the T + cyclohexene gas phase system [3]. In this system, one scavengeable thermal reaction product is cyclohexane-t which results largely from thermal addition of T to the double bond to form a cyclohexyl-t radical. This radical then abstracts a hydrogen atom from the bulk system to form cyclohexane-t. The cyclohexane-t yield exhibited identical scavenger plateaus with sulfur dioxide and oxygen scavenging. Ethylene-t and butadiene-t are primarily high energy products from the unimolecular decomposition of excited cyclohexene-t formed by direct substitution [4]. The ethylene-t yield exhibited identical scavenger plateaus with sulfur dioxide and oxygen scavenging. The butadiene-t yield was unaffected by sulfur dioxide scavenging but increased by nearly 50% with oxygen scavenging. This anomalous increase in the butadiene-t yield with oxygen scavenging is similar to an anomalous increase in the ethylene-t yield with O₂ scavenging that was reported by Urch and Welch in the T + ethane system [5].

The anomalous ethylene-t increase in the T + ethane system was explained by Baker and Wolfgang [6]. Apparently, in the absence of O_2 , radiation-produced H atoms were being scavenged by the ethylene-t formed by hot tritium reactions. This reduced the ethylene-t yield in unscavenged systems. When O_2 was added, the radiation-produced H atoms were scavenged by the more efficient O_2 and the ethylene-t yield increased from essentially zero to its "hot" value.

A similar explanation of the anomalous increase in the butadiene-t yield in the oxygen scavenged T + cyclohexene system was not intuitively obvious at that time for two reasons: (1) In the T + ethane case, selective depletion of the ethylene-t molecules by H atoms may be solely dependent upon ethylene-t being the only alkene in the system. The rate constant (at 25°C) for H atom addition to a double bond to form an alkyl radical is usually an order of magnitude greater than the rate constant of abstraction of a hydrogen atom to form H_2 [7]. In the T + cyclohexene case, the butadiene-t molecules might be "protected" from radiation produced H atoms by the unlabeled cyclohexene molecules. The number of unlabeled cyclohexene molecules was larger than the number of butadiene-t molecules by a factor of 10^7 to 10^8 . This should have made H-atom addition to cyclohexene the predominant reaction in the system even if the rate constant for H-atom addition to butadiene is larger than the rate constant for H atom addition to cyclohexene by a factor of 100 [3]. (2) SO_2 was as efficient as O_2 in scavenging products of thermalized radicals in the T + cyclohexene and T + trans-butene systems [3]. Sulfur dioxide was not as efficient as O_2 in removing thermalized tritium atoms. In the T + n-butane system, the thermal T atoms react by abstracting a hydrogen atom to form HT.

The HT yield from tritium reactions with n-butane was decreased more with O_2 scavenging than with SO_2 scavenging. In addition, the HT yield exhibited a scavenger plateau with O_2 scavenging but no plateau with SO_2 scavenging. SO_2 removed some but not all of the thermal tritium atoms [3]. SO_2 scavenging is thus expected to remove some but not all of the radiation produced H atoms in the T + cyclohexene system. If the butadiene-t yield in the T + cyclohexene system increases with O_2 scavenging due to removal of all radiation produced H atoms, the butadiene-t yield should increase to some extent with SO_2 scavenging. Because the butadiene-t yield did not increase with SO_2 scavenging, the hypothesis that the butadiene-t yield rises to its "hot" value only with O_2 scavenging was discredited.

Recently, we attempted to calculate the maximum effect of radiation produced H atoms on the butadiene-t yield in the T + cyclohexene system. The problem involves the competitive reactions with hydrogen atoms of butadiene-t vs. cyclohexene, cyclohexene plus O_2 , and cyclohexene plus SO_2 . The pertinent rate constants are shown in Table I. The butadiene-t yield is extremely sensitive to the yield of H atoms from radiation damage. The "hot" butadiene-t yield is only reduced by about one third when the H atoms are not removed by O_2 . The yield of H atoms simply cannot be estimated to the degree of certainty required to demonstrate convincingly that the butadiene-t yield is or is not reduced by H atom reactions. Similarly, an uncertain amount of unlabeled butadiene is also present in the system from radiation damage [8]. The unlabeled butadiene would also "protect" the butadiene-t yield by competing for H atoms with equal efficiency. Since the calculations were inconclusive and the preceding intuitive arguments actually depended upon the calculations, further experiments were necessary.

We decided to determine how the butadiene-t yield from T + cyclohexene reactions varied with scavenging by butadiene-d₆ and by hydrogen sulfide. Butadiene and butadiene/O₂ mixtures had been successfully employed as scavengers in recoil chlorine systems [9]. H₂S has been employed as a scavenger in radiolysis [10], photolysis [11], and recently in recoil tritium experiments [12]. A priori we compared O₂, SO₂, H₂S and butadiene-d₆ by the criteria for a good scavenger proposed by Hawke and Wolfgang [2], namely:

1. A Scavenger Must React Avidly With The Atoms And Radicals To Be Removed, Preferably With A Collision Efficiency Near Unity.

It may then be used in sufficiently low concentrations so as not to interfere with the hot or other primary processes being studied. The pertinent rate constants are shown in Table I and II. We use methyl radicals as representative of all alkyl radicals; the rate constants of other alkyl radicals are not known for all potential scavengers. Abstraction is the reaction whose product is H₂ and CH₄ when hydrogen atoms and methyl radicals are respectively one of the reactants. Addition is the reaction which removes H-atoms or methyl radicals from the system by forming a new radical (via radical addition to the double bond of the scavenger) or by forming a stable molecule such as CH₃SO₂. From these tables, two things are clear: a) Butadiene-t is the most reactive hydrocarbon in the T + cyclohexene system. It could be selectively depleted not only by hydrogen atoms but by also by radiolysis produced radicals. However, a "radical contribution" to the anomalous increase in the butadiene-t yield in the oxygen scavenged T + cyclohexene system can safely be neglected. Both O₂ and SO₂ are orders of magnitude more reactive with radicals than butadiene-t. b) Butadiene-d₆ is the most efficient of the four scavengers for removing H atoms. The effect of butadiene-d₆ scavenging on the butadiene-t yield should be unambiguous.

2. A Scavenger Should Be Inert With Respect To The Bulk Reagent.

Rapid cis-trans isomerization of either cis- or trans-2-butene is known to be catalyzed by H_2S and SO_2 in the presence of radiation [23,24]. Compensation can be made for the resultant cis/trans equilibrium mixture in recoil tritium studies of 2-butene with H_2S scavenging [12]. We have found that SO_2 catalyzes a 1% conversion of trans-2-butene to cis-2-butene in recoil tritium studies of trans-2-butene. This is comparable to the radiolysis value [24]. The radiation-induced addition of H_2S to olefins is known to occur with enormous G values [25]. The resultant sulfur-containing species would not be eluted in the normal radio-gas-chromatographic analysis. Therefore, this effect cannot be directly measured in recoil tritium systems. We have monitored instead the area of the cyclohexene mass peak. This showed that within experimental error cyclohexene was not depleted by radiation-induced reactions with H_2S in the T + cyclohexene system. Similar measurements showed butadiene- d_6 to be unreactive with cyclohexene, as expected. Reactions of O_2 with the bulk cyclohexene system have been noted [3].

3. Products Of The Scavenging Reaction Should Not React Further, Or If They Do, Such Reaction Should Be Controllable.

No problems of this sort have been encountered previously with these scavengers.

4. A Gas Phase Scavenger Must Have An Adequate Vapor Pressure At The Temperature In Question.

Oxygen easily satisfies this criteria. The vapor pressure at room temperature for SO_2 is more than two atmospheres, for H_2S more than twenty atmospheres; and for butadiene more than two atmospheres [26].

5. Furthermore, It Is Highly Desirable But Not Always Essential That The Scavenged Species Be Detectable.

H_2S reacts with thermalized tritium atoms and alkyl and alkenyl radicals to form HT and the corresponding alkanes and alkenes, respectively. These species are readily detectable. The primary products of scavenging with butadiene- d_6 are tritiated alkenyl radicals. If these alkenyl radicals abstract a hydrogen atom from the bulk system, the resultant alkene is readily assayed and identified as a scavenger product. However, if the alkenyl radical decomposes or begins a radical addition chain with the bulk system, a unique scavenger product cannot be determined. The primary products from O_2 and SO_2 scavenging are not readily assayed in the conventional radio-gas-chromatographic analysis used for recoil tritium experiments. In addition, these primary products may react further with the bulk system or other radicals. As yet, there is no evidence that such further reaction results in products which might be mistaken for the yield of a hot reaction.

EXPERIMENTAL

The experimental procedure employed was similar to that described previously for sample preparation [27]. The typical sample was a 1720 Pyrex glass capsule (2 cm o.d., 14 ml internal volume) to which 5.0 cm of cyclohexene, 1.5 cm 3He and varying amounts of scavenger had been added (at room temperature). The irradiations were for 10 min at a flux of $2.7 \times 10^{11} \text{ n cm}^{-2} \text{ sec}^{-1}$ in the Berkeley Campus nuclear reactor. Radiation damage due to the recoils following the $^3He(n,p)T$ reaction was less than 2%. The gas-phase tritium-labeled products were separated by gas chromatography and counted in a flow proportional counter. Well resolved peaks were obtained by a gas chromatographic method similar to that employed by Ting and Rowland [27] except when butadiene- d_6 was used as a scavenger.

Butadiene- d_5T , DT and other deuterated tritium-labeled hydrocarbons were formed from $T + \text{butadiene-}d_6$ reactions. In principle, the deuterated compounds could be separated from the protonated compounds by gas chromatography and the $T + \text{cyclohexene}$ reaction products could be determined unambiguously. In practice, this would be extremely difficult. We settled for separating butadiene- d_5t (C_4D_5T) from butadiene- t (C_4H_5T) on a 20 ft. saturated $AgNO_3$ /ethylene glycol column. For all other products with four or fewer carbon atoms, the sum of the contributions from $T + \text{cyclohexene}$ and $T + \text{butadiene-}d_6$ reactions was determined. Cyclohexane- t and cyclohexene- t resulted only from $T + \text{cyclohexene}$ reactions. The details of this analysis will be given elsewhere [28]. The recovery of "polymer- t " has been described previously [29]. All data reported represents the average of the yields from two identical samples that agreed to within 5% on major products.

RESULTS AND DISCUSSION

The effect of the four scavengers on the cyclohexane- t yield is shown in Fig. 1. Three trends should be noted: (1) The cyclohexane- t yield does not exhibit a scavenger plateau with butadiene- d_6 scavenging. Butadiene- d_6 is less efficient than O_2 and SO_2 in removing the cyclohexyl- t radicals. This is consistent with the trend of the rate constants in Table II. (2) The ethylene- t yield increases slightly with H_2S scavenging. This confirms a small contribution to the ethylene- t from thermal or radical processes that is demonstrated by the decrease in ethylene- t yield with O_2 and SO_2 scavenging. The effect of butadiene- d_6 scavenging on the ethylene- t yield was not determined. The contribution to the ethylene- t yield from $T + \text{cyclohexene}$ reactions was not separated from the contribution from $T + \text{butadiene-}d_6$ reactions. (3) The

cyclohexane-t yield increases dramatically with H_2S scavenging. This confirms a cyclohexyl-t radical intermediate. As predicted by Table II, abstraction of a hydrogen from H_2S is a faster reaction for cyclohexyl-t radicals than either the addition or abstraction reaction with cyclohexene. H_2S intercepts the cyclohexyl-t radicals before they react with cyclohexene to form tritiated hydrocarbons, C_{12} or greater, through radical chain addition. These species are counted as "polymer-t". While the "polymer-t" data do not indicate the chemical composition of the tritiated products, crude separations by volatility may be performed. Low (molecular weight) "polymer-t" is backflushed from the chromatographic columns. Medium "polymer-t" is washed from a 10 ft. stainless steel tube (1/16" o.d.) connecting the sample breaker to the chromatographic columns. Heavy "polymer-t" is washed from the walls of the capsule in which the recoil tritium reaction took place [29]. The relative abundance of activity in each volatility grouping changes with the scavenger employed. The "polymer-t" was distributed 20% in the medium and 70% in the heavy groupings for O_2 scavenged samples and 2% in the medium and 97% in the heavy groupings for SO_2 scavenged samples. The lowered "polymer-t" volatility with SO_2 scavenging is consistent with the expected formation of scavenged species of higher molecular weight and/or lower volatility with SO_2 than O_2 . The total "polymer-t" yield decreased from 74 relative to cyclohexene-t as 100 for the unscavenged samples to 36 for H_2S scavenged samples. The cyclohexane-t yield increased from 32 to 112, and the yields of other minor products also increased with H_2S scavenging. This is surprising because the increase in cyclohexane-t yield should come at the expense of the "polymer-t" yield. This may indicate that recovery of "polymer-t" is not complete [29]. No correction was necessary for ^{35}S activity (from the

$^{34}\text{S}(n,\gamma)^{35}\text{S}$ reaction which could be included in our measurements as the ^{35}S was incorporated into the "polymer-t". Even with the highest SO_2 or H_2S pressures, the total ^{35}S activity is less than 1% of the "polymer-t" activity. The total "polymer-t" exhibits a scavenger plateau with O_2 , SO_2 and H_2S scavenging. When butadiene- d_6 is used as a scavenger the total "polymer-t" yield increases with increasing butadiene- d_6 concentration. This is as expected because butadiene- d_6 is a major source of "polymer-t" and only the sum of the "polymer-t" from $\text{T} + \text{butadiene-}\text{d}_6$ and $\text{T} + \text{cyclohexene}$ reactions could be determined.

Figure 2 shows that the butadiene-t yield increases with butadiene- d_6 scavenging. The scavenger plateau is identical to that obtained with O_2 scavenging. This supports the hypothesis that the butadiene-t yield is selectively depleted by radiolysis-produced H atoms in the absence of O_2 . The butadiene-t yield decreases with H_2S scavenging. Table I shows that H_2S is inefficient as an H atom scavenger. But H_2S is a source of H atoms through radiolysis [30]. The increase in H atom concentration with no increase in the ability to scavenge H atoms (relative to butadiene-t) would further reduce the butadiene-t yield. Now shown in Fig. 2 is a dramatic increase in the 1-butene-t yield with H_2S scavenging. 1-butenyl radicals would be formed by H atom addition to butadiene-t. These radicals could abstract an H atom from the bulk system (probably from H_2S) to form 1-butene-t.

The hypothesis that butadiene-t is selectively depleted by reactions with H atoms from the radiolysis of H_2S and/or cyclohexene is supported by the dual scavenger data in Fig. 2. The solid data points show the effect on the butadiene-t yield when two scavengers are used simultaneously. All samples

were scavenged by butadiene- d_6 . The butadiene- d_6 /(cyclohexene + butadiene- d_6) ratio was constant at 0.15. Varying amounts of H_2S , O_2 or SO_2 were added as indicated. The butadiene-t yield is the same for each of the combinations of scavengers and is slightly higher than for O_2 or butadiene- d_6 used solely [31]. When the T + cyclohexene system is simultaneously scavenged by H_2S and butadiene- d_6 , the butadiene- d_6 "protects" the butadiene-t from being selectively depleted by reactions with H atoms from H_2S and cyclohexene. The butadiene-t yield thus rises to its "hot" value. Except for butadiene-t, H_2S exhibits normal scavenger behavior in the T + cyclohexene system. The yield of products with a radical precursor increases with H_2S scavenging and a scavenger plateau is observed. When the T + cyclohexene system is simultaneously scavenged by SO_2 and butadiene- d_6 , the butadiene- d_6 protects the butadiene-t from being selectively depleted by reactions with radiolysis-produced H atoms. Sulfur dioxide is not sufficiently reactive to protect butadiene-t from H atoms. However, SO_2 is sufficiently reactive to protect the less reactive unsaturated tritiated hydrocarbons. These yields are the same for both O_2 and SO_2 scavenging. Sulfur dioxide exhibits normal scavenger behavior in alkene systems for all products except butadiene-t. When O_2 and butadiene- d_6 are simultaneously used as scavengers in the T + cyclohexene system, both O_2 and butadiene- d_6 protect the butadiene-t yield from the radiolysis-produced H atoms. There is no anomalous behavior with O_2 scavenging.

We conclude that: (1) The "hot" butadiene-t value from T + cyclohexene reactions can only be determined with O_2 or butadiene- d_6 scavenging. Previous workers did not determine the "hot" butadiene-t yield [4]. (2) Oxygen is the most efficient single scavenger for both thermalized T (and H) atoms and

tritiated radicals. Butadiene- d_6 / SO_2 dual scavenging is nearly as efficient as O_2 for both radicals and H atoms. Although butadiene- d_6 / SO_2 scavenging requires a more complex analytical scheme, use of these scavengers may be preferable to O_2 in cases where O_2 reacts with the parent alkene [3]. (3) Sulfur dioxide and hydrogen sulfide exhibit normal scavenger behavior in T + alkene systems for all products except butadiene-t. This may limit their use to systems where butadiene-t is not a major product.

ACKNOWLEDGEMENTS

We are grateful for the continued able assistance of Fred Vogelsberg who has built and maintained our equipment. We would like to thank Robert McCracken for help in the irradiations.

FOOTNOTES AND REFERENCES

*Work performed under the auspices of the U. S. Atomic Energy Commission.

- [1] R. L. Wolfgang, "Progress in Reaction Kinetics", III (G. Porter, ed.) Pergamon, Oxford, 1965.
- [2] J. Hawke and R. L. Wolfgang, *Radiochimica Acta* 14, 116 (1970).
- [3] D. C. Fee, S. S. Markowitz, and J. K. Garland, *Radiochimica Acta* (1972) (in press).
- [4] R. W. Weeks and J. K. Garland, *J. Phys. Chem.* 73, 2508 (1969); R. W. Weeks and J. K. Garland, *J. Am. Chem. Soc.* 93, 2380 (1971).
- [5] D. S. Urch and M. J. Welch, *Trans. Faraday Soc.* 62, 388 (1966).
- [6] R. T. K. Baker and R. L. Wolfgang, *Trans. Faraday Soc.* 65, 1842 (1969).
- [7] G. R. Wolley and R. J. Cvetanovic, *J. Chem. Phys.* 50, 4697 (1969); R. J. Cvetanovic and L. C. Doyle, *J. Chem. Phys.* 50, 4705 (1969).
- [8] Less than 3% of the gamma radiolysis products of cyclohexene result from ring fission. See G. R. Freeman, *Can. J. Chem.* 38, 1043 (1960).
- [9] Z. B. Alfassi and S. Amiel, *Radiochimica Acta* 15, 201 (1971); C. M. Wai and F. S. Rowland, *J. Phys. Chem.* 24, 434 (1970).
- [10] W. A. Pryor and U. Tonellato, *J. Phys. Chem.* 73, 850 (1969).
- [11] R. Lesclaux, S. Searles, L. W. Sieck, and P. Ausloos, *J. Chem. Phys.* 53, 3336 (1970).
- [12] R. Kushner and F. S. Rowland, *J. Phys. Chem.* 75, 3771 (1971).
- [13] H. W. Melville and J. C. Robb, *Proc. Roy. Soc.* A202, 181 (1950).
- [14] R. W. Getzinger and G. L. Schott, *J. Chem. Phys.* 43, 3237 (1965); P. Riesz and E. J. Hart, *J. Phys. Chem.* 63, 858 (1959).
- [15] K. R. Jennings and R. J. Cvetanovic, *J. Chem. Phys.* 35, 1233 (1961).
- [16] R. W. Fair and B. A. Thrush, *Trans. Faraday Soc.* 65, 1550 (1969).

- [17] H. A. Kazmi and D. J. LeRoy, Can. J. Chem. 42, 1145 (1964).
- [18] A. Good and J. C. J. Thynne, Trans. Faraday Soc. 63, 2708 (1967).
- [19] M. I. Christie, Proc. Roy. Soc. A244, 411 (1958).
- [20] N. Imai and O. Toyama, Bull. Chem. Soc. Japan 33, 652 (1960).
- [21] R. J. Cvetanovic and R. S. Irwin, J. Chem. Phys. 46, 1694 (1967).
- [22] W. M. Jackson, J. R. McNesby, and B. de B. Darwent, J. Chem. Phys. 37, 1610 (1962).
- [23] N. Imai and O. Toyama, Bull. Chem. Soc. Japan 38, 224 (1965),
- [24] W. Ando, K. Sugimoto, and S. Oae, Bull. Chem. Soc. Japan 38, 226 (1965).
- [25] K. Sugimoto, W. Ando, and S. Oae, Bull. Chem. Soc. Japan 38, 221 (1965).
K. Sugimoto, W. Ando, and S. Oae, Bull. Chem. Soc. Japan 37, 365 (1964).
- [26] Handbook of Chemistry and Physics, 49th Edition, Chemical Rubber Company, Cleveland, 1968.
- [27] C. T. Ting and F. S. Rowland, J. Phys. Chem. 74, 445 (1970).
- [28] D. C. Fee and S. S. Markowitz, to be submitted to Analytical Chemistry.
- [29] J. K. Garland, Anal. Letters 1, 273 (1968).
- [30] G. Meissner and A. Henglein, Z. Naturforschg 20b, 1005 (1965).
- [31] With dual scavenging, the butadiene-t yield increases by at most ten percent over the yield for O_2 or butadiene- d_6 used solely. Because this is only twice the uncertainty of each individual data point, the increase may not be significant. It should be noted, however, that Baker and Wolfgang (Ref. 6) reported a similar percent increase in the C_2H_3T yield (from T + ethane reactions) when O_2 and C_2D_4 were employed simultaneously as scavengers. If the increase is real it may indicate that the combination of scavengers is slightly more efficient in removing thermal H atoms than either scavenger used solely.

Table I. Hydrogen Atom Reaction Rate Constants at 25°C.

Reactant	Addition		Abstraction	
	[10 ⁹ cm ³ mole ⁻¹ sec ⁻¹]		[10 ⁹ cm ³ mole ⁻¹ sec ⁻¹]	
butadiene	1500	ref. (7)	22	(7)
cyclohexene	600	(13)	n.d. ^a	
O ₂	300	(14)	— ^b	
ethylene	200	(7)	13	(7)
trans-2-butene	180	(7)	21	(15)
H ₂ S	—		160	(7)
SO ₂	6	(16)	—	
n-butane	—		0.6	(17)

^aNot determined.^bNot applicable.

Table II. Methyl Radical Reaction Rate Constants at 25°C.

Reactant	Addition		Abstraction	
	[10 ⁶ cm ³ mole ⁻¹ sec ⁻¹]		[10 ⁶ cm ³ mole ⁻¹ sec ⁻¹]	
O ₂	15,000	ref. (18,19)	— ^b	
SO ₂	5,000	(18)	—	
H ₂ S	—		3,000	(20)
butadiene	64	(21)	n.d. ^a	
ethylene	1.2	(21)	0.02	(21)
trans-2-butene	0.3	(21)	0.2	(21)
cyclohexene	n.d.		n.d.	
n-butane	—		0.004	(22)

^aNot determined.

^bNot applicable.

FIGURE CAPTIONS

Fig. 1. The effects of O_2 , SO_2 , H_2S , and C_4D_6 on the ethylene-t yield and the cyclohexane-t yield from T + cyclohexene reactions. Product yields are listed relative to the cyclohexene-t yield as 100. The O_2 and SO_2 points are from Ref. 3. The zero scavenger data point and the 5 mole % scavenger data point have been connected with a line for clarity. We do not imply that the variation yield with added scavenger is linear in this region.

Fig. 2. The effects of O_2 , SO_2 , H_2S , C_4D_6 and C_4D_6 plus O_2 , C_4D_6 plus SO_2 , C_4D_6 plus H_2S on the butadiene-t yield from T + cyclohexene reactions. Product yields are listed relative to the cyclohexene-t yield as 100. The O_2 and SO_2 single scavenger points are from Ref. 3. The solid data points represent C_4D_6 plus another scavenger used jointly. The abscissa in this case does not include the moles of C_4D_6 . The zero scavenger data point and the 5 mole % scavenger data point have been connected with a line for clarity. We do not imply that the variation of yield with added scavenger is linear in this region.

XBL 726 - 3100

Fig. 1

XBL726-3101

Fig. 2

LEGAL NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

TECHNICAL INFORMATION DIVISION
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720