# Reactivity and Reversibility in the Reaction of Thiyl Radicals with Olefins[1]

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The reaction of thiyl radicals with olefin to yield the composite radical C·, was found to be reversible in solution, so that in the addition of methanethiol to cis-2-butene at 60° in the presence of azoisobutyronitrile (AIBN), the trans isomer appears in the unreacted olefin. It was found that the rate constant for the formation of trans-2-butene from the composite radical is 80 times the rate constant for product formation by transfer with thiol. The rate constant for cis-2-butene formation is 20 times the rate constant for product formation. Using gas chromatography, a rapid technique was developed for determining the relative reactivities of various monomers toward thiyl radical by competitive reactions, taking into account the reversibility of the attack step. The relative reactivities of a number of monomers toward thiyl radicals were determined and related to reactivities found by other workers.

The free radical addition of thiols to olefins is a reaction which has been studied[2] extensively and is considered to involve the chain propagating steps

$$RS· + CH_2=CHR' \longrightarrow RSCH_2—\dot{C}HR' \quad (1)$$

$$RSCH_2—\dot{C}HR' + HSR \longrightarrow$$
$$RSCH_2—CH_2R' + RS· \quad (2)$$
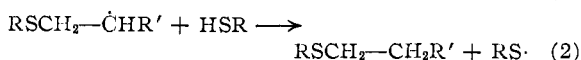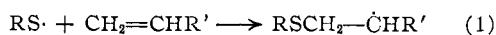
In a previous paper from this Laboratory[3] evidence was discussed that reactions which are essentially the reverse of 2, i.e., the abstraction of hydrogen from hydrocarbons by thiyl radicals can occur with ease in certain systems. There is also good reason to believe that reaction 1 may be reversible as well. In studying the addition of methanethiol to isobutylene, propylene and ethylene in the gas phase, Sivertz[4] found negative over-all activation energies of 8 to 9 kcal. Experiments in these laboratories[5] demonstrated this reversibility in solution by the rapid isomerization of unreacted olefin during the addition of methanethiol to cis- and trans-2-butene at 60°. The isomerization of 2-butene by thiophenol in solution also has been reported subsequently by Sivertz.[6]

This paper presents more detailed data on this reversibility, and also on the relative reactivity of different olefins toward thiyl radicals, taking this reversibility into account.

Results and Discussion

Isomerization of cis- and trans-2-Butene by Thiols.—If we assume that when a thiyl radical attacks the 2-butene the composite radical thus formed loses its stereochemistry rapidly by rotation about the C–C bond, we can write the scheme for the reaction as shown in (3).

The intermediate composite radical (designated below as C·) presumably can regenerate either the cis- or trans-olefin depending upon its conformation at the time of thiyl radical loss.

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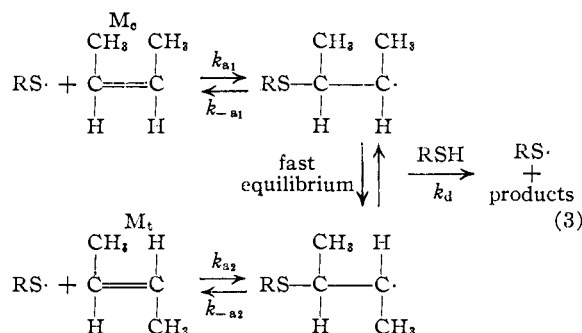
(2) For a review and pertinent references cf. C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, pp. 313–326.

(3) C. Walling and R. Rabinowitz, THIS JOURNAL, 81, 1137 (1959).

(4) C. Sivertz, W. Andrews, W. Elsdon and K. Graham, J. Polymer Sci., 19, 587 (1956).

(5) Reference 2, p. 323.

(6) R. H. Pallen and C. Sivertz, Can. J. Chem., 35, 723 (1957).

Assuming that we start with the pure cis isomer, then at the beginning of the reaction, when none of the trans isomer has as yet formed

$$k_{a_2}/k_d = \Delta(M_t)/\log(RSH)_0(RSH)^{-1} = R_1 \quad (4)$$

since

$$\Delta(M_c) - \Delta(RSH) = \Delta(M_t) \quad (5)$$

We can therefore plot apparent values of R_1 against the fraction of RSH which has reacted at different times, and extrapolation to zero reaction will give the true value of k_{-a_2}/k_d.

Similarly, starting with pure trans-2-butene, a plot of

$$\Delta(M_c)/\log(RSH)_0(RSH)^{-1} = R_2 \quad (6)$$

against the fraction of RSH which has reacted at different times and extrapolation to zero reaction will give the true value of k_{-a_1}/k_d.

Samples of a reaction mixture consisting of pure cis-2-butene, n-butane (a non-reacting internal standard), methanethiol and azobisisobutyronitrile (AIBN), were heated to 60° as described in the Experimental section. These were then periodically analyzed by gas chromatography. The results of two such experiments are shown in Table I (expts. 21 and 25). The values of R_1 are plotted against $\Delta(RSH)/(RSH)_0$ in Fig. 1. A least squares treatment yields values of 83.7 and 86.1 for k_{-a_2}/k_d from experiments 21 and 25, respectively.

Similar experiments (24 and 27) carried out on pure trans-2-butene yielded the results in Fig. 2. The values obtained for k_{-a_1}/kd are 18.8 and 20.7.

We see, therefore, that the decomposition of the composite radical into thiyl radical and olefin is very rapid compared to the transfer reaction with thiol, being about 80 times faster for the trans and 20 times faster for the cis isomer at 60°. In the event that our assumption of equilibrium between radical conformations is not correct, the extent of reversibility must be even larger.
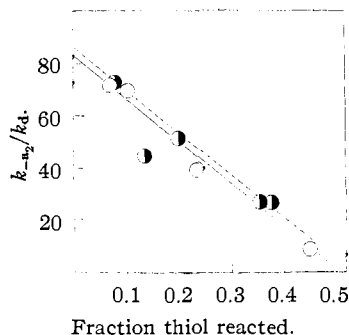
Fig. 1.—Determination of k_{-a_2}/k_d in addition of methanethiol to cis-2-butene: open circles, expt. 21; half-black circles, expt. 25.

It is of interest to compare this reaction with the addition of bromotrichloromethane to the 2-butenes, studied by Skell and Woodworth.[7] The addition proceeds by a chain mechanism similar to that of the thiol addition, in which the trichloromethyl radical is the chain carrier. The radical attack on the olefin is not reversible in this case since no isomerization of the butene occurs. However, both the cis- and the trans-2-butenes give an identical mixture of addition products, showing that the composite radical loses its stereochemistry completely,

TABLE I

ISOMERIZATION OF 2-BUTENES BY METHANETHIOL

	trans	cis	RSH	R_1	Δ (RSH)/ (RSH)$_0$
			millimoles		
		Experiment 21			
Initial		42.8	69.2		
21-3	4.75	33.5	64.7	72.0	0.065
21-5	6.12	2.9	35.4	9.15	.449
21-6	7.28	28.6	62.3	69.9	.100
21-7	10.8	15.7	52.9	40.1	.235
		Experiment 25			
Initial		40.3	44.4		
25-1	6.0	30.8	40.9	73.5	0.079
25-2	12.2	12.5	28.8	28.3	.376
25-4	12.5	11.75	28.6	28.4	.356
25-5	8.10	27.8	40.0	42.5	.135
25-6	11.7	19.6	35.4	52.0	.203

Effect of Reversibility on Competitive Addition Reactions.—The relative reactivities of olefins toward thiyl radicals can be determined by using a competitive reaction technique. In this treatment, if it is assumed that olefin disappears only by addition of thiyl radical, and if this addition is not reversible, then the rates at which the olefins disappear can be related directly to the rate constants of the attack by thiyl radical k_{a_1} and k_{a_2} via the usual equation

$$P = \frac{\log (M_1)_0/(M_1)}{\log (M_2)_0/(M_2)} = \frac{k_{a_1}}{k_{a_2}} \qquad (7)$$

where $(M_1)_0$ and (M_1) are initial and final concentrations of olefin M_1, and $(M_2)_0$ and (M_2) are initial and final concentrations of olefin M_2. If the thiyl radical addition is reversible we must consider a scheme where the reactions of each olefin

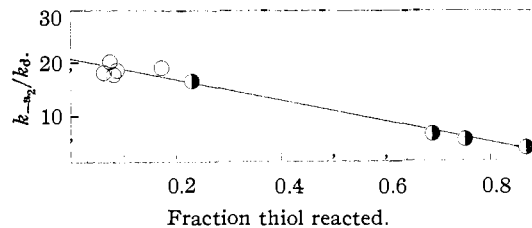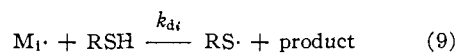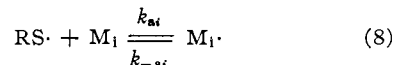(7) P. S. Skell and R. C. Woodworth, THIS JOURNAL, 77, 4638 (1955).

Fig. 2.—Determination of k_{-a_1}/k_d in addition of methanethiol to trans-2-butene: open circles, expt. 24; half-black circles, expt. 27.

are governed by the sequence

$$RS\cdot + M_1 \underset{k_{-ai}}{\overset{k_{ai}}{\rightleftharpoons}} M_1\cdot \qquad (8)$$

$$M_1\cdot + RSH \xrightarrow{k_{di}} RS\cdot + product \qquad (9)$$

For two olefins reacting in competition we obtain

$$P = \frac{\log (M_1)_0/(M_1)}{\log (M_2)_0/(M_2)} = \frac{k_{a_1}[1 + k_{-a_2}/k_{d_2}(RSH)]}{k_{a_2}[1 + k_{-a_1}/k_{d_1}(RSH)]} \qquad (10)$$

providing reactions are carried out in the presence of enough thiol so that its concentration remains effectively constant. In the case that M_1 adds RS· irreversibly, 10 reduces to

$$P = (k_{a_1}/k_{a_2})(1 + k_{-a_2}/k_{d_2}[RSH]) \qquad (11)$$

If 11 is obeyed, a plot of P vs. $1/[RSH]$ should be linear, and extrapolation to $1/[RSH] = 0$ yields k_{a_1}/k_{a_2}. If 10 is obeyed, such a plot becomes a hyperbola, but one not normally asymptotic to the zero axis, so a similar extrapolation should be possible. Application of this treatment to some actual systems was made.

Samples of a reaction mixture consisting of approximately equimolar amounts of 1-decene, trans-β-methylstyrene, toluene, about 1 mole % AIBN and varying amounts of dodecanethiol were irradiated in an ice–water-bath with a G. E. sunlamp for about 30 minutes. In those samples in which a low thiol concentration was required, ethyl phthalate was used as a diluent. After the reaction, samples were analyzed as described in the Experimental part. The results are shown in Table II. A plot of P against $1/[RSH]$ is shown in Fig. 3. In this figure M_1 is trans-β-methylstyrene and M_2 is 1-decene.
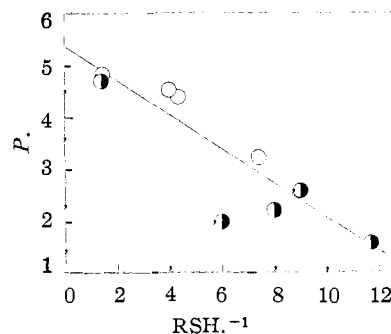

Fig. 3.—Effect of thiol concentration on relative reactivities of β-methylstyrene, M_1, and 1-decene, M_2: open circles, expt. 50 et seq.; half-black circles, expt. 60 et seq.

Although there is considerable scattering in the experimental points, which is due mainly to the in-

accuracy involved in analyzing high boiling materials quantitatively in the gas chromatography apparatus used, it is nevertheless apparent that there is little difference between the values of P at $1/[RSH] = 0$ and $1/[RSH] = 2$. The values are 5.4 and 4.8, respectively, a difference of about 10%.

A similar experiment was performed using methyl acrylate and 1-octene at 0 and 60°. Results are shown in Table III and values of P are plotted against $1/(RSH)$ in Fig. 4. It can be seen
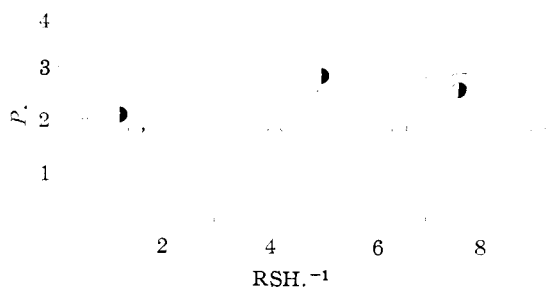

Fig. 4.—Effect of thiol concentration on relative reactivities of methyl acrylate, M_1, and 1-octene, M_2: open circles, 0°; half-black circles, 60°.

that at 0° this line is approximately parallel to the x-axis, thus showing little dependence on thiol concentration. The experiments at 60°, although less accurate, nevertheless indicate that there is no gross dependence of relative rates on thiol concentration. The fact that the relative reactivity of the methyl acrylate seems to be slightly greater at 60° than at 0° has no significance.

The failure to observe any pronounced curvature in the plots of Figs. 3 and 4 suggests that our extrapolations to $1/(RSH) = 0$ are valid, and accordingly give k_{a_1}/k_{a_2} as intended. Actually, it seems plausible that reversibility is less serious in either of these systems than in the case of 2-butene, since addition to β-methylstyrene yields a highly resonance stabilized composite radical, and addition to 1-substituted olefins is generally more rapid, more exothermic, and less reversible than to 1,2-disubstituted olefins.[8]

Relative Reactivities of Olefins toward Dodecanethiol.—The small effect of thiol concentration on P in the experiments just described makes it appear worthwhile to report a series of measurements on a variety of olefins made at a single thiol concentration at 60° using equation 7, since the relative reactivities so calculated should measure k_{a_1}/k_{a_2} to a reasonable approximation.

In a typical experiment, samples of a mixture consisting of approximately equimolar quantities of about five monomers, a non-reacting standard material, about 1 mole % initiator, and enough dodecanethiol to make its concentration greater than 0.5 molar, were heated in a 60° thermostat for varying periods of time. The samples were then analyzed for unreacted olefin by gas chromatography as described in the Experimental part. The concentrations of the various olefins now were compared with their concentrations before reac-

(8) See, for example, the ceiling temperatures observed in the copolymerization of SO₂ with terminal and non-terminal olefins, ref. 2, pp. 223-228.

TABLE II

COMPETITIVE REACTION OF β-METHYLSTYRENE AND
1-DODECENE WITH DODECANETHIOL AT 0°

	┌──log $[M]_0[M]^{-1}$──┐			
Expt.	M_1(Me Styrene)	M_2(decene)	P	$[RSH]^{-1}$
52	0.2952	0.0672	4.40	4.30
54	.4203	.0916	4.58	3.95
55	.4945	.1529	3.23	7.38
58	.5786	.0828	4.79	1.42
63	.5391	.2052	2.63	9.15
64	.3560	.1593	2.24	8.02
65	.3766	.2375	1.59	11.7
66	.6395	.3150	2.03	6.00
68	.2274	.0480	4.75	1.41

TABLE III

COMPETITIVE REACTION OF METHYL ACRYLATE AND
1-OCTENE WITH DODECANETHIOL

	┌──log $[M_0][M]^{-1}$──┐			
Expt.	M_1(methyl acrylate)	M_2(1-octene)	P	$[RSH]^{-1}$
		0°		
71	0.1467	0.0874	1.68	1.505
72	.1018	.0615	1.65	4.03
73	.1274	.0668	1.90	6.51
74	.1341	.0759	1.77	9.22
		60°		
81	0.2472	0.1179	2.10	1.20
82	.4698	.1835	2.56	7.68
83	.6294	.2442	2.84	5.08

tions, and relative rates then were determined from eq. 7. The results are shown in Table IV. The high values for methyl acrylate and methyl methacrylate in experiments 3 and 5 probably are due to some propagation and perhaps some co-polymerization of these monomers. The values for relative reactivities found in experiments 80 and 93 were obtained in a large excess of thiol, where these effects are not as pronounced.

Some observations can be made from the data given in Table V. 1. The high reactivity of styrene shows that reactivity is increased if the resultant composite radical is stabilized by resonance. 2. Electron-supplying groups on the olefin increase the rate as is demonstrated by 2-methyl-1-butene and vinyl butyl ether. Electron-withdrawing groups, on the other hand, decrease the rate as is shown by allyl cyanide. Presumably this is due to the sort of resonance stabilization of the transition states suggested by Walling, Seymour and Wolfstirn,[9] the RS· radical acting as an electron acceptor. 3. Cyclopentene is more reactive than cyclohexene. 4. Terminal double bonds are more reactive than internal ones. Thus, cyclic olefins and dichloroethylene show decreased reactivity.

These observations are in general agreement with those made by Kharasch and co-workers[10] in the addition of CCl_3· radicals to olefins and with those found by Szwarc and co-workers in their work with methyl radicals.[11] One expected ex-

(9) C. Walling, D. Seymour and K. B. Wolfstirn, THIS JOURNAL, 70, 2559 (1948).

(10) M. S. Kharasch and H. N. Friedlander, J. Org. Chem., 14, 239 (1949); M. S. Kharasch and M. Sage, ibid., 14, 537 (1949); M. S. Kharasch, E. Simon and W. Nudenberg, ibid., 18, 328 (1953).

(11) M. Szwarc, J. Polymer Sci., 16, 367 (1955); F. Leavitt, M. Levy, M. Szwarc and V. Stannett, THIS JOURNAL, 77, 5493 (1955);

TABLE IV

RELATIVE REACTIVITIES OF OLEFINS TOWARD DODECANETHIOL AT 60°

Olefin	1,2	3	4	5	100	Other	Average[e]
Styrene	17						17 ± 3
β-Methylstyrene						5.5[a]	5.5 ± 0.5
Vinyl butyl ether				3.86			3.9 ± .4
Methyl methacrylate		8.45				2.4[b]	2.4 ± .2[d]
Methyl acrylate		3.73		3.93		1.95[c]	2.04 ± .2
Allyl alcohol				1.50			1.5 ± .15
2-Methyl-1-butene			1.20				1.2 ± .08
1-Octene	1.00	1.00	1.00	1.00	1.00	1.00	1.00 (stnd.)
Allylbenzene	0.99						0.99 ± 0.08
Vinyl acetate		0.796			0.853		.81 ± .04
Allyl chloride			0.723				.72 ± .04
Cyclopentene			0.636				.64 ± .04
Allyl acetate	0.570			0.67	0.536		.59 ± .06
Allyl cyanide				0.37			.37 ± .05
Cyclohexene	0.301	0.198			0.258		.25 ± .05
cis-Dichloroethylene	<0.2		Very low				<.2

[a] Experiments 50 and 60 at 0°.   [b] Experiment 93.   [c] Experiment 80.   [d] Values from expts. 3 and 5 not included; see text.   [e] Experimental errors given are mean deviations of several determinations.

ception is 2 above, since methyl radicals appear, if anything, to act as weak electron donors. They also accord with the extensive data on olefin reactivity derived from copolymerization results,[12] particularly (as might be expected) those involving radicals with strong electron-withdrawing groups, and thus having electron acceptor properties. This correspondence, in turn makes it seem likely that equation 7 is here a valid approximation.

Some General Comments on Thiyl Radical Reactions.—Our results certainly substantiate the rather easy reversibility of thiyl radical additions in some systems. Since the additions are significantly exothermic ($\Delta H = -14$ kcal./mole),[2] they must be processes involving considerable loss of entropy. The results of this and the preceding paper[3] also suggest that reactions involving thiyl radicals, in general, occur with extreme ease if exothermic and, if endothermic, require little activation energy in excess of ΔH for the over-all process. This conclusion certainly lends plausibility to the idea that many of the varied reactions between sulfur and organic molecules which occur at high temperatures involve at least in part, species such as RS· or RS$_x$· which attack CH bonds, add to unsaturation, and are in turn regenerated by other hydrogen abstraction processes.

Again, since thiols are readily oxidized by ionic oxidants such as polyvalent metal ions they could perhaps act as carriers to permit the attack of such oxidants on organic molecules, e.g.

$$M^{++} + RSH \longrightarrow M^{+} + RS· + H^{+}$$
$$RS· + HR^{1} \longrightarrow RSH + R·^{1}$$
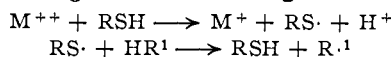
and could conceivably play such a role in some enzyme systems.

Experimental

Materials.—All solvents were best commerical grades used without further purification.

R. P. Buckley, F. Leavitt and M. Szwarc, ibid., **78**, 5557 (1956); R. P. Buckley and M. Szwarc, ibid., **78**, 5696 (1956); M. Gazith and M. Szwarc, ibid., **79**, 3339 (1957); A. Rajenbach and M. Szwarc, ibid., **79**, 6343 (1957).

(12) F. R. Mayo and C. Walling, Chem. Revs., **46**, 191 (1950); also ref. 2, pp. 117–140.

n-Dodecanethiol (Matheson), allyl alcohol (Eastman), allyl chloride (Eastman), allyl cyanide (Eastman), 2-methyl-1-butene (Phillips) were used without further purification.

n-Octene (b.p. 122–123°), vinyl acetate (b.p. 71–72°), vinyl butyl ether (b.p. 93–93.5°), methyl acrylate (b.p. 74.5–76°) and methyl methacrylate (b.p. 100°), were distilled through a short column and center cuts were collected. Styrene was distilled through a short column at 50 mm. pressure. All polymerizable olefins were stored at −20°.

Cyclohexene was distilled through a 2-foot helix-packed column and a fraction boiling at 82.0° was collected.

Cyclopentene was of unknown origin, b.p. 44°, n^{25}D 1.4189.

Methanethiol, n-butane, cis- and trans-2-butene were obtained in gas cylinders from Matheson.

Allyl acetate was washed with 5% sodium bicarbonate solution, saturated calcium chloride solution, and then dried with sodium sulfate. The product was distilled through a 30-cm. helix packed column at aspirator pressure and a center cut was collected, n^{27}D 1.4004.

Allylbenzene was prepared by the method of Hershberg,[13] b.p. 156.7–157.3°.

cis-β-Methylstyrene was prepared by the reduction of methylphenylacetylene by the method of Mixer, Heck, Winstein and Young.[14] Methylphenylacetylene was prepared by the method of Campbell and O'Connor,[15] b.p. 61–64° (15 mm.), n^{25}D 1.5346.

trans-β-Methylstyrene was prepared by the thermal dehydration of phenylethylcarbinol. Phenylethylcarbinol was distilled to remove benzaldehyde and then dropped onto fused KHSO₄ in a three-necked flask fitted with a condenser. The distillate consisted of starting material and trans-β-methylstyrene containing about 5% cis isomer by gas chromatographic analysis. This mixture was distilled through a spinning band column, b. p. 70–74° (15 mm.), n^{25}D 1.5463.

Isomerization of 2-Butene.—In a typical experiment (expt. 21), 2.40 g. (42.8 mmoles) of cis-2-butene, 2.40 g. (58.9 mmoles) of n-butane and 3.32 g. (69.2 mmoles) of methanethiol were condensed on a vacuum line into a vessel consisting of a large bulb and a series of small vials; 4.1 mg. (0.025 mmole) AIBN was added and the mixture was degassed two times at 0.03 mm. using liquid nitrogen. The solution was then divided among the vials, and these were sealed off and placed in a 60.0° thermostat and withdrawn periodically. Unreacted olefin, thiol and butane now were distilled out at room temperature into a Dry Ice trap. A sample of the distillate (about 2 cc. after vaporization in the injection syringe) was then injected into a Perkin-Elmer model 154 vapor fractometer. An A and a C column were

(13) E. B. Hershberg, Helv. Chim. Acta, **17**, 351 (1934).

(14) R. Y. Mixer, R. F. Heck, S. Winstein and W. G. Young, THIS JOURNAL, **75**, 4094 (1953).

(15) K. M. Campbell and M. J. O'Connor, ibid., **61**, 2897 (1939).
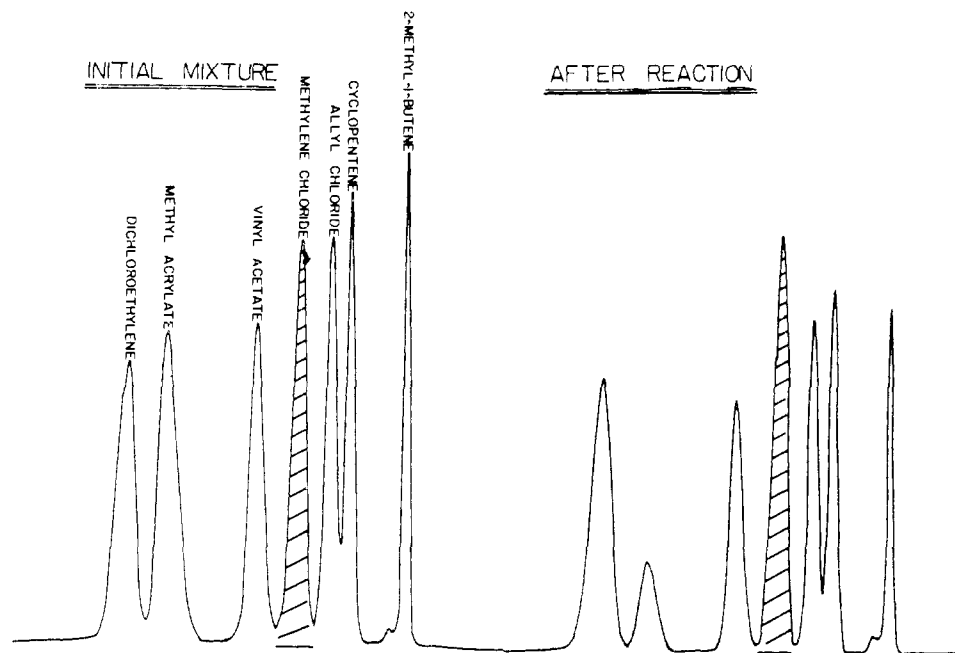
Fig. 5.—Gas chromatogram illustrating simultaneous determination of relative reactivities of six olefins toward dodecane thiol.

used in series at room temperature, and helium at 25 lb. pressure was used as the carrier. The A column is a 6-foot column containing nonyl phthalate supported on Celite. The C column is the same length and contains silicone grease on Celite. The butane, *trans*-2-butene, *cis*-2-butene and methanethiol appeared in that order and within 16 minutes. The amount of material in the sample is given by the expression $h/h_0 \times M$ where h is the peak height of the material relative to butane, h_0 is the relative peak height of the material before the reaction and M is the amount of material orginally present. The amounts of material calculated from the relative peak heights of thiol and original olefin are given in Table I. Isomerized olefin was calculated by difference.

Competitive Reaction of β-Methylstyrene and 1-Decene with Dodecanethiol at 0°.—In a typical experiment (expt. 50) a reaction mixture was prepared consisting of 1.11 g. (7.93 mmoles) of 1-decene, 1.44 g. (13.60 mmoles) of *trans-β*-methylstyrene, 0.908 g. (9.86 mmoles) of toluene and 35 mg. of AIBN. By adding varying amounts of dodecanethiol and ethyl phthalate to portions of this mixture, samples were obtained having the thiol concentrations shown in Table II. These samples were suspended in a stirred ice-water-bath and irradiated with a G. E. sunlamp for about 30 minutes through the Pyrex container. Unreacted olefin and toluene then were distilled out at 1 mm. pressure using a Dry Ice condenser. The distillate was analyzed on a Per-kin–Elmer model 154 vapor fractometer using an "A" column at 150°. The ratio of initial to final concentration of monomer was calculated from the peak heights relative to toluene as described above for expt. 21.

Competitive Reaction of Methyl Acrylate and 1-Octene with Dodecanethiol.—The procedure was similar to that described above. Analysis of the unreacted olefin was by gas chromatography using an "A" column at 100°. The internal standard used was benzene.

Determination of Relative Reactivities of Olefins at 60°.—Experiment 4 is typical. Here 2 ml. each of 2-methyl-1-butene, cyclopentene, allyl chloride, methylene chloride, vinyl acetate, methyl acrylate and *cis*-dichloroethylene were mixed with 25 ml. of dodecanethiol and 160 mg. of AIBN. A 2-ml. portion of this mixture was distilled rapidly at 55 mm. pressure into a Dry Ice trap and the distillate was analyzed by gas chromatography as described above using an "A" column at 65°. Other 2-ml. samples were sealed into vials and heated in a 60.0° thermostat for periods of 0.5 to 5 hours. Samples were then distilled and analyzed as above. Figure 5 shows a typical chromatogram.

It is to be noted that the experimental technique described here for determining relative reactivities did not require any weighings or measurements other than determinations of relative peak heights before and after reaction on a chromatogram. This method may be contrasted with the relatively very tedious techniques used by other workers[9,10] for similar experiments. These techniques involved actual analyses of individual products of competitive reactions and were thus restricted to the comparison of two monomers at a time.

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