5. It is suggested that the dark bromination of ethylene in carbon tetrachloride proceeds mainly through a bromine hydrate and that the concentration of this hydrate increases as the temperature is lowered from 25 to 0°.

6. The olefins brominate at very different rates in carbon tetrachloride.

7. Light increases the rates of bromination of the olefins but decreases the relative differences between them.

8. Studies in the reactions of olefins with halogens may clear up many of the questions unanswered by researches on the photochemical reactions of halogens with hydrogen.

9. The methods used for following the courses of the bromination were (A) color comparison with a standard bromine solution, (B) titration of the bromine.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 35]

THE RELATIVE RATES OF ABSORPTION OF THE GASEOUS BUTENES INTO SULFURIC ACID[1]

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In 1909 Michael and Brunel[3] published data on the proportions of the butenes which were absorbed by sulfuric acid in Hempel pipets after definite periods of shaking. From inspection of the results they gave certain approximate figures for the relative rates of absorption of the three isomers.

Calculations from the data of Michael and Brunel show that in each experiment the rate of solution of the butene was approximately proportional to the quantity undissolved. The following table gives the values of K calculated for the separate experiments where $K = 1/t \ln 1/(1-x)$, t = minutes the pipet was shaken, and x = fraction of olefin dissolved at time t.

The following conclusions can be drawn regarding the rates of solution of olefin gases when shaken with sulfuric acid in Hempel pipets.

1. A pure butene was absorbed at a rate approximately proportioned to the gas undissolved (see Experiments 1, 2, 5, 6 and 7. The high initial rate of solution in 5 may perhaps be attributed to traces of *iso*butene).

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[3] Michael and Brunel, *Am. Chem. J.*, **41**, 118 (1909).

Table I

Absorption of the Butenes into Sulfuric Acid in Hempel Pipets

1. Pure *iso*butene, 58.6% sulfuric acid, 21–22°

t	X[a]	$K \times 10^{-3}$
0	0	..
20	0.59	45
40	.88	53
60	.97	58
120	.98	33
	Av. =	47

2. Pure *iso*butene, 58.6% sulfuric acid, 28–29°

t	X	$K \times 10^{-3}$
0	0	..
10	0.69	117
20	.89	110
40	.97	87
	Av. =	105

3. Mixture, 51.8% of *iso*butene + 48.2% of 2-butene, 58.6% sulfuric acid, 21–22°

t	X[b]	$K \times 10^{-3}$
0	..	..
20	0.40	26
60	.82	29
100	.92	25
	Av. =	27

4. Mixture, 57.5% of *iso*butene + 42.5% of 2-butene, 58.6% sulfuric acid, 28–29°

t	X[b]	$K \times 10^{-3}$
0	..	..
15	0.45	40
30	.65	35
45	.87	45
60	.95	50
	Av. =	43

5. Pure 2-butene, 58.6% sulfuric acid, 28–29°

t	X	$K \times 10^{-3}$
0	..	..
10	0.012	(1.3)
20	.017	0.85
40	.020	.50
150	.048	.33
175	.083	.49
	Av. =	.54

6. Pure 2-butene, 76% sulfuric acid, 29–30°

t	X	$K \times 10^{-3}$
0	..	..
20	0.18	10
40	.33	10
60	.44	9.7
80	.55	10
	Av. =	10

7. Pure 1-butene, 76% sulfuric acid, 29–30°

t	X	$K \times 10^{-3}$
0	..	..
20	0.09	4.8
40	.17	4.7
60	.27	5.3
80	.35	5.4
	Av. =	5.0

[a] Recalculated, taking the proportion soluble in strong sulfuric acid as 100%.

[b] The 2-butene dissolved so much more slowly than the *iso*butene that it was counted merely as a diluent of the latter.

It is true that the values for K are only approximately constant in any one experiment. Nevertheless, the averages of these values become quite significant for the different gases.

It should be emphasized that Michael and Brunel did not carry out these experiments with a view to calculating absorption coefficients and it is a tribute to the accuracy of the data that this can be done with results so satisfactory as those given above.

2. When diluted with non-reacting gas, *iso*butene was absorbed at a rate proportional to the *iso*butene undissolved. The magnitude of the rate was, however, cut down in approximate proportion to the dilution (see Expts. 3 and 4).

This accords with the results from certain experiments of mine on the rates of absorption of olefins by sulfuric acid in rotating tubes at constant volume. The rate of solution was very closely proportional to the partial pressure of the olefin even when admixed with varying quantities of air.

The rates of absorption of the butenes into sulfuric acid may therefore be fairly well compared by their absorption coefficients, K, Table II, from which effects of changes in the gaseous volume, partial pressure of the olefin and time of shaking have been largely eliminated.

TABLE II

ABSORPTION COEFFICIENTS K FOR THE THREE BUTENES INTO SULFURIC ACID IN HEMPEL PIPETS

No.	Olefin	Concn. of H_2SO_4, %	Temp., °C.	Absorption coefficient, K[a]
1	*Iso*butene (pure)	58.6	21–22	47×10^{-3}
2	*Iso*butene (pure)	58.6	28–29	105×10^{-3}
3	*Iso*butene (57.5%)	58.6	21–22	46×10^{-3}
4	*Iso*butene (51.8%)	58.6	28–29	75×10^{-3}
5	2-Butene (pure)	58.6	28–29	0.54×10^{-3}
6	2-Butene (pure)	76	29–30	10.0×10^{-3}
7	1-Butene (pure)	76	29–30	5.0×10^{-3}

[a] Calculated for the pure gas at atmospheric pressure.

TABLE III

RELATIVE RATES OF ABSORPTION OF THE BUTENES

From Table II			Relative rates of absorption into sulfuric acid[a]	
$\frac{K_2(\text{2-butene})}{K_1(\text{1-butene})}$	at 29–30°	2	1-butene	1
$\frac{K_3(\textit{iso}\text{butene})}{K_2(\text{2-butene})}$	at 28–29°	140–195	2-butene	2
			*iso*butene	280–390

[a] This last comparison will not hold broadly if the relative rates depend upon the concentration of the acid or the temperature. The effects of these two conditions on the absorption of olefins into sulfuric acid are now being investigated experimentally.

Summary

Calculations on the relative rates of absorption of the three butenes into sulfuric acid have been made from the experimental data of Michael and Brunel.

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