propanes. Normally, the first aliquot of each sample, consisting of about 50% of the total, was analyzed on this column. Two or more of the other columns were then used for auxiliary purposes.

(d) 30'DMS: 30-ft column of 25% dimethylsulfolane on 30–50 mesh activated alumina. The order of the retention times is similar to that of the 50'DMS, but the actual time required is much shorter. With a flow rate of 25 ml/min, it takes more than 10 hr for the elution of oxygenated compounds such as alcohols.

Two more columns, a 50-ft di-*n*-butyl phthalate (50'DBP) and a 50-ft tri-*o*-tolyl phosphate (50'TTP), were also used during the preliminary runs. They were discarded later because the oxygenated compounds emerged too quickly, making impossible the isolation of the individual peaks of the fluorocyclopropanes.

Analysis of Mixtures from Competition Experiments. The relative reactivities of different olefins were obtained from the observed yields of the appropriate radioactive product(s) for each olefin, corrected for the mole ratio of the olefins in the mixture. The mole ratios were measured by thermal conductivity response, calibrated for each molecule, as measured during the gas chromatographic analyses.

Kinetics of the Hydroxymercuration of Olefins[1]

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Abstract: The kinetics of the hydroxymercuration of 20 olefins and substituted (hydroxy, chloro, and cyano) olefins, $Hg^{2+} + {>}C{=}C{<} + H_2O \rightarrow [Hg{\geqslant}C{-}C{\leqslant}OH]^+ + H^+$, have been determined in aqueous perchloric acid solution. The rate law in each case was found to be rate $= k[Hg^{2+}][{>}C{=}C{<}]$, where the values of k, $\Delta H^{\ddagger}$, and $\Delta S^{\ddagger}$ for ethylene are $5.1 \times 10^3\ M^{-1}\ sec^{-1}$ (at 25°), 9.2 kcal/mole, and -10 eu, respectively. The rate of hydroxymercuration was found to be independent of the H^+ concentration (between 0.001 and 0.1 M), to increase with the $NaClO_4$ concentration, and, contrary to earlier reports, to be unaffected by H_2O_2 and by O_2. For substituted olefins an excellent correlation between log k and Taft's σ^* ($\rho^* = -3.3$) was observed, suggesting a transition state with considerable carbonium ion character. No evidence was found for mercury(II)–olefin π complex (mercurinium ion) intermediates and, while the possibility of such intermediates is not excluded, the data do permit certain limits to be placed upon their stabilities and concentrations.

The addition of oxy salts of mercury to olefins (oxymercuration) to give β-oxyorganomercury(II) derivatives is a well-known reaction,[2–5] which finds no really close parallel in the chemistry of other metals.[6–8] The reaction in aqueous solutions containing uncomplexed mercury(II) (hydroxymercuration) is, typically

$$Hg^{2+} + CH_2{=}CHR + H_2O \longrightarrow [HgCH_2CHROH]^+ + H^+ \qquad (1)$$

where R = H, alkyl, or aryl. While the stoichiometry and stereochemistry of the reaction have been extensively investigated,[3,5] there are virtually no reliable data[9] concerning its kinetics, apparently because the reaction in solutions containing uncomplexed Hg^{2+} is generally too fast for conventional rate measurements.

In this paper we report the results of such kinetic measurements on the hydroxymercuration of ethylene and some 20 other olefins and substituted (hydroxy, chloro, and cyano) olefins, made by means of the stopped-flow method. The measurements were made, in part, with a view to seeking evidence for a mercury(II)–olefin π complex (mercurinium ion), which has been postulated as an intermediate in oxymercuration and deoxymercuration reactions.[10,11] but no such evidence was obtained.

Of related interest to the present study are earlier reports on the kinetics of oxymercuration of olefins in solutions containing complexed mercury(II) (*e.g.*, chloride, acetate, and pyridine complexes)[12] on the kinetics of acid-induced deoxymercuration[11,13] and on the kinetics of the oxidation of olefins by thallium(III) for which a mechanism involving an oxythallation step, analogous to oxymercuration, has been proposed.[7,8]

Experimental Section

Materials. The gaseous olefins (ethylene, propylene, 1-butene, isobutene, *cis*-2-butene, and *trans*-2-butene) were all Matheson CP grade reagents. The absence of volatile impurities was con-

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[1] This work was supported by grants from the National Science Foundation, the Advanced Research Projects Agency, and the Petroleum Research Fund, administered by the American Chemical Society.

[2] K. Hofmann and J. Sand, *Chem. Ber.*, **33**, 1340, 2692 (1900).

[3] J. Chatt, *Chem. Rev.*, **48**, 7 (1951).

[4] G. F. Wright, *Ann. N. Y. Acad. Sci.*, **65**, 436 (1957).

[5] N. S. Zefirov, *Russ. Chem. Rev.*, **34**, 527 (1965).

[6] Possible exceptions to this generalization are to be found in the reactions of certain thallium(III) salts with olefins.[7,8]

[7] P. M. Henry, *J. Am. Chem. Soc.*, **87**, 990, 4424 (1965); **88**, 1597 (1966).

[8] R. R. Grinstead, *J. Org. Chem.*, **26**, 238 (1961); C. B. Anderson and S. Winstein, *ibid.*, **28**, 605 (1963); H. J. Kabbe, *Ann.*, **656**, 204 (1962).

[9] In the light of the results reported in this paper it would appear that most of the earlier rate measurements on the hydroxymercuration of olefins in solutions containing uncomplexed Hg^{2+}, such as those of P. Brandt and O. Plum [*Acta Chem. Scand.*, **7**, 97 (1953)], refer to physically transport limited, rather than chemically determined, rates.

[10] H. Lucas, F. Hepner, and S. Winstein, *J. Am. Chem. Soc.*, **61**, 3102 (1939).

[11] See, for example, M. M. Kreevoy and M. A. Turner, *J. Org. Chem.*, **30**, 373 (1965), and references cited therein.

[12] E. R. Allen, J. Cartledge, M. M. Taylor, and J. F. Tipper, *J. Phys. Chem.*, **63**, 1437, 1442 (1959).

[13] K. Ichikawa, K. Nishimura, and S. Takayama, *J. Org. Chem.*, **30**, 1593 (1965).

firmed in each case by gas chromatography using a 20-ft β,β'-oxydipropionitrile (60–80 mesh Chromosorb P) column.

The following reagents were obtained commercially and purified by drying over calcium chloride or sodium sulfate, followed by distillation with a spinning band column: 1-buten-4-ol, bp 113.0–113.5° (lit.[14a] bp 113°); 1-buten-3-ol, bp 96.0 (lit.[14a] bp 97.3°); 1-propen-3-ol, bp 97° (lit.[14a] bp 97°); 1-penten-3-ol, bp 114–115° (lit.[14a] bp 114–116°; 1-penten-4-ol, bp 116° (lit.[14a] bp 115°); 1-penten-5-ol, bp 141° (lit.[14a] bp 139–142°); 1-hexen-6-ol, bp 124–126°; 2-cyclohexen-1-ol, bp 165–166° (lit.[14a] bp 164–166°); allyl cyanide, bp 119° (lit.[14a] bp 119°); allyl chloride, bp 45° (lit.[14a] bp 45°). Cyclohexene was Matheson Coleman and Bell chromatoquality. *cis*-2-Butene-1,4-diol was recrystallized from methanol, mp 10.7° (lit.[14b] mp 11.0°). *cis*- and *trans*-2-buten-1-ol could not be completely separated, but several mixtures of varying composition (ranging from 1:1.7 to 1:4.0), determined gas chromatographically, were prepared by fractional distillation.

Solutions of sodium perchlorate and mercury(II) perchlorate were prepared by neutralizing reagent grade sodium carbonate and mercury(II) oxide with reagent grade perchloric acid. Solutions of mercury(I) perchlorate were prepared by shaking solutions of mercury(II) perchlorate with metallic mercury. The water used for the preparation of all the solutions was redistilled from alkaline permanganate in an all-Pyrex still.

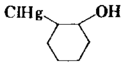
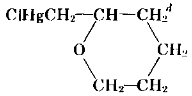
Preparation and Isolation of Products. The hydroxymercuration products were prepared by slowly adding 0.1 mole of the olefin (from a gas buret in the case of gaseous olefins, otherwise as a dilute solution) and, simultaneously, an equivalent amount of NaOH, to 100 ml of a 0.01 *N* $HClO_4$ solution containing 0.1 mole of $Hg(ClO_4)_2$. The pH of the solution was then raised to 11 with NaOH, 0.1 mole of an alkali halide (NaCl or NaI) added, and the excess NaOH neutralized with CO_2. On standing at 0°, the corresponding organomercury(II) halide separated out and was purified by recrystallization. The products obtained in this way are described in Table I.

Two of the reaction products, yielded by the above procedure, presumably 2,4-dihydroxybutylmercury(II) iodide (from 1-buten-4-ol) and 2-chloromercurymethyltetrahydrofuran (from 1-penten-5-ol) were obtained as oils which could not be crystallized or characterized. On reduction with sodium amalgam, which is known to effect demercuration by reductive cleavage of the mercury–carbon bond, the expected products, namely 1,3-butanediol, bp 205° (lit.[14a] bp 205°), and 2-methyltetrahydrofuran, bp 78–80° (lit.[14a] bp 78–80°), both identified by nmr spectroscopy, were obtained.

The product oil obtained from the reaction of 1-penten-5-ol was also reacted with I_2 and the resulting product (presumably 2-iodomethyltetrahydrofuran) hydrolyzed with dilute NaOH to yield, on distillation, 2-hydroxymethyltetrahydrofuran, bp 80° (20 mm) (lit.[14a] bp 80 (20 mm)), identified by nmr spectroscopy.

Kinetic Measurements. Most of the rate measurements were made on reactions having half-lives less than 30 sec, using the stopped-flow apparatus, previously described,[15] equipped with a Beckman deuterium lamp and an EMI 6256 photomultiplier. The formation of the hydroxymercuration product is accompanied by an increase in absorbance in the range 200–230 mμ (Figure 1) which was used to follow the reaction. In a few cases a pH indicator, cresol red, was added and the change in its absorbance at 520 mμ, owing to the production of H^+ (eq 1), was used to follow the reaction. Typically, one of the two solutions in the stopped-flow experiments contained, before mixing, 10^{-5} to 5.0×10^{-4} *M* $Hg(ClO_4)_2$ and the other at least a tenfold higher concentration of the olefin (10^{-3} to 10^{-1} *M*). The concentrations of $HClO_4$ (0.001–0.1 *M*) and of $NaClO_4$ (0–0.1 *M*) were the same in both solutions, the total ionic strength generally being 0.1 *M*, except in those experiments in which the ionic strength was deliberately varied. Temperature control of the solutions in the stopped-flow apparatus was within about ±0.2°, except for temperatures below 5° which were controlled to within ±1°. The reactant concentrations were so adjusted that the total change in absorption coefficient accompany-

Table I. Selected Oxymercuration Products

Olefin	Recovered product	Yield,[a] %	Mp, °C Found	Mp, °C Lit.	Analysis,[b] % Found C	Found H	Found Hg	Calculated C	Calculated H	Calculated Hg	Mass no. of parent peak[c] Found	Calcd
$CH_2{=}CH_2$	$ClHgCH_2CH_2OH$	80	153–154	153–155[14e]	8.75	1.61	71.60	8.54	1.79	71.36	282	282
cis-$CH_3CH{=}CHCH_3$	*threo*-$IHgCH(CH_3)CH(OH)CH_3$	50	79–80	78–80[14d]	11.91	2.32	50.11	11.99	2.26	50.07	402	402
trans-$CH_3CH{=}CHCH_3$	*erythro*-$IHgCH(CH_3)CH(OH)CH_3$	60	76	76[14d]	12.11	2.32	50.00	11.99	2.26	50.07		
Cyclohexene		90	151	151[14e]	21.62	3.24	59.62	21.50	3.31	59.85	336	336
$CH_2{=}CHCH_2OH$	$IHgCH_2CH(OH)CH_2(OH)$	70	76	80[14f]	8.96	1.62	49.73	8.95	1.75	49.83	404	404
$CH_2{=}CHCH(OH)CH_2CH_3$	$IHgCH_2CH(OH)CH(OH)CH_2CH_3$[d]	95	127 dec	. . .	13.83	2.63	46.54	13.94	2.58	46.58	432	432
$CH_2{=}CHCH_2CH_2CH_2CH_2OH$		90	88	. . .	21.36	3.32	59.70	21.49	3.31	59.84	336	336

[a] Based on recovery of recrystallized product. Spectral titrations similar to those described in Figure 2 suggest that primary yield is close to 100%. [b] Performed by Alfred Bernhardt, Mulheim, Germany. [c] Measured on AEI MS 9 dual focus mass spectrometer. Value reported is for species containing ^{202}Hg and ^{35}Cl or ^{127}I. [d] Not previously reported.

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(14) (a) "Handbook of Chemistry and Physics," Chemical Rubber Publishing Co., Cleveland, Ohio, 1967; (b) W. M. Smith, Jr., K. C. Eberly, E. E. Hanson, and J. L. Binder, *J. Am. Chem. Soc.*, **78**, 626 (1956); (c) K. A. Hofmann and J. Sand, *Chem. Ber.*, **33**, 1353 (1900); (d) M. M. Kreevoy, L. L. Schlager, and J. C. Ware, *Trans. Faraday Soc.*, **58**, 2433 (1962); (e) A. G. Brook and G. F. Wright, *Can. J. Res.*, **B28**, 623 (1950); (f) K. A. Hofmann and J. Sand, *Chem. Ber.*, **33**, 2698 (1900).

(15) N. Sutin and G. L. Dulz, *Inorg. Chem.*, **2**, 917 (1963); J. P. Candlin, J. Halpern, and D. L. Trimm, *J. Am. Chem. Soc.*, **86**, 1019 (1964).

ing the reaction was small enough (<0.1 cm^{-1}) that the transmittance changes recorded on the oscillograms were proportional to the concentration changes.

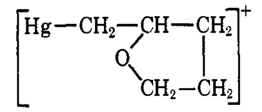
A few of the experiments, notably with *cis*-2-butene-1,4-diol, were slow enough ($t_{1/2} > 30$ sec) so that their rates could be measured conventionally using a Cary 14 spectrophotometer, as were the rates of reaction of olefins with Hg_2^{2+}. The latter experiments were performed by shaking a suspension of mercury in a solution of the olefin and mercurous perchlorate (to prevent supersaturation) and withdrawing samples of the solution periodically for analysis, using the intense absorption band of Hg_2^{2+} at 236.5 mμ (ϵ_{max} 2.8 × 10^4) to follow the reaction. Except for a few of the fastest reactions, the measured rate constants were generally reproducible to ±5%.

Results and Discussion

Stoichiometry and Stereochemistry. Many earlier investigations[3-5,16] of the stoichiometry and stereochemistry of the oxymercuration of olefins have established that (i) the stoichiometry of the over-all reaction is essentially in accord with eq 1, (ii) that addition proceeds in a Markovnikov manner, and (III) that, at least for simple unhindered olefins such as cyclohexene, and *cis*- and *trans*-2-butene, addition is *trans*.[17] The last two points were not further explored in this work except to confirm, for a representative number of the reactions examined, that (with the two exceptions noted below), the expected hydroxymercuration products were obtained under the conditions of our experiments (see Table I).

Departures from the stoichiometry described by eq 1 were noted for two of the reactions examined, namely, those of 1-penten-5-ol and 1-hexen-6-ol. Instead of the diol products of hydroxymercuration, these olefins yielded the internal ethers (I) and (II), respectively, according to the reactions

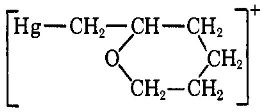
$CH_2{=}CHCH_2CH_2CH_2OH + Hg^{2+} \longrightarrow$



$+ H^+$ (2)

I

$CH_2{=}CHCH_2CH_2CH_2CH_2OH + Hg^{2+} \longrightarrow$



$+ H^+$ (3)

II

Other examples of the formation of tetrahydrofuran derivatives, analogous to I, by oxymercuration of unsaturated alcohols, have previously been reported.[18]

Spectral Changes and Spectral Titrations. Further evidence that the stoichiometries of the reactions studied are quantitatively described by eq 1, 2, and 3 were obtained from the spectral titrations described below.

The formation of the oxymercuration product, in each case, was accompanied by a spectral change similar to that in Figure 1, corresponding to a marked increase in absorbance below 250 mμ. Sepctral titration experiments, in which the absorbance change accompanying the incremental addition of olefin to a solution of Hg^{2+} was measured, were performed for a representative selection of the olefins studied (propene, allyl alcohol, 1-buten-4-ol, 1-penten-3-ol, and 1-penten-4-ol) and yielded, in each case, results similar to those in Figure 2, which demonstrate quantitatively the formation of 1 mole of the oxymercurial per mole of added olefin.

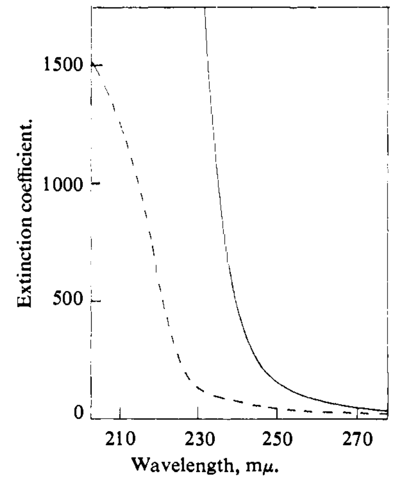


Figure 1. Absorption spectra of Hg^{2+} (- - - -) and of $HgCH(CH_3)CH(OH)CH_3^+$ (———), formed by hydroxymercuration of *trans*-2-butene. (Absorption of *trans*-2-butene is negligible above 220 mμ.)

Analogous spectral titration experiments were performed in which increments of olefin were added to solutions of mercury(II) perchlorate containing cresol red indicator and the accompanying increase of the H^+ concentration was determined from the absorbance change of the indicator. These yielded, in every case (for 14 of the olefins studied), results similar to those in Figure 2. Exactly one H^+ ion was produced for each molecule of olefin added until all the mercury(II) was consumed. The results of both titration experiments are in accord with the stoichiometries described in eq 1–3. They further demonstrate that the equilibria corresponding to these reactions under our conditions lie far to the right and that there is no appreciable accumulation of species such as mercurinium ion[5] (mercury(II)–olefin complexes), whose formation is not accompanied by release of H^+.

General Kinetic Behavior. All the reactions examined exhibited kinetic behavior corresponding to the second-order rate law

$$\frac{d[Hg{>}C{-}C{<}OH^+]}{dt} = \frac{d[H^+]}{dt} = k[Hg^{2+}][{>}C{=}C{<}] \quad (4)$$

Under the conditions employed, with the olefin generally in substantial excess over mercury(II), the observed kinetics were pseudo first order, *i.e.*

$$d[Hg{>}C{-}C{<}OH^+]/dt = k'[Hg^{2+}] \quad (5)$$

where

$$k' = k[{>}C{=}C{<}] \quad (6)$$

Values of k' were computed from the slopes of first-order plots derived, in turn, from oscillograms such as that in Figure 3. The first-order dependence of k' on the olefin concentration, confirmed for each olefin at least one temperature, is depicted in Figure 4. Values of k are listed in Table II, and the activation parameters

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[16] M. M. Kreevoy, L. L. Schaleger, and J. C. Ware, *Trans. Faraday Soc.*, **58**, 2433 (1962).

[17] *cis* addition, possibly dictated by steric considerations, is observed for certain bicycloolefins such as norbornene.[5]

[18] R. Adams, F. L. Roman, and W. N. Sperry, *J. Am. Chem. Soc.*, **44**, 1781 (1922); J. Sand, *Ann.*, **329**, 135 (1903).

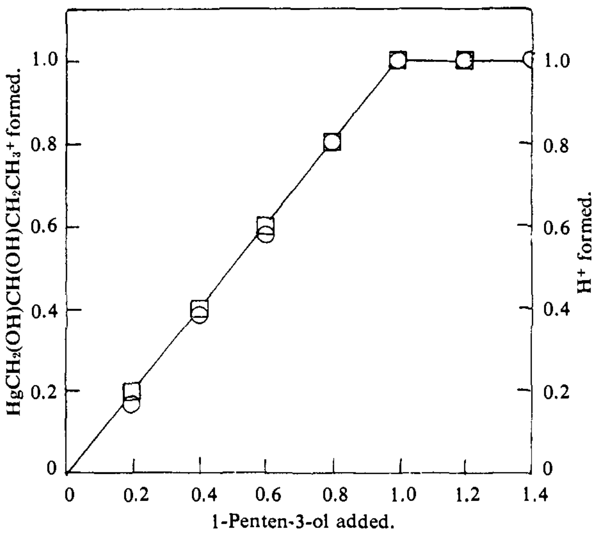

Figure 2. Titration of Hg^{2+} with 1-penten-3-ol, showing moles of $HgCH_2CH(OH)CH(OH)CH_2CH_3^+$ (○) and of H^+ (□) formed. All concentrations are expressed relative to the initial mercury(II) concentration.

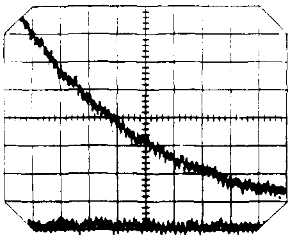

Figure 3. Typical oscillograms showing transmittance change at 220 mμ for the reaction between mercury(II) and ethylene at 20°: 1.0×10^{-4} M $Hg(ClO_4)_2$; 1.02×10^{-3} M C_2H_4; 0.01 M $HClO_4$; 0.09 M $NaClO_4$ (time scale, 50 msec per division).

computed from these data (which yielded in every case a good Arrhenius plot) are listed in Table III.

The rates of reaction of several olefins (1-buten-3-ol, 1-pentene-3-ol, and *cis*-2-butene-1,4-diol) were also measured by following (spectrally, using cresol red indicator) the formation of H^+ during the reaction. The rates thus obtained were in good agreement with those determined from the formation of the oxymercuration product (Table II), confirming that the proposed reaction stoichiometry is maintained throughout the reaction. The rates of reaction of allyl chloride and allyl cyanide were measured only by the indicator method.

The rate of one reaction (that of *cis*-2-butene-1,4-diol), measured in D_2O, was found to be indistinguishable from that in H_2O (Table II).

Contrary to earlier reports[19] of catalysis of oxymercuration by oxygen and hydrogen peroxide, the rate of hydroxymercuration of *trans*-2-butene was found to be unaffected by the addition of up to 3.3×10^{-4} M O_2 or of up to 7.5×10^{-3} M H_2O_2. Absence of O_2 catalysis was also confirmed for the reaction of allyl alcohol.

Effect of Hydrogen Ion. The rates of hydroxymercuration of the following olefins were found to be independent of the H^+ concentration over the ranges indicated: ethylene (0.01–0.1 M H^+); *trans*-2-butene (0.001–0.1 M H^+); 1-penten-4-ol (0.01–0.1 M H^+); 1-cyclohexen-3-ol (0.005–0.1 M H^+).

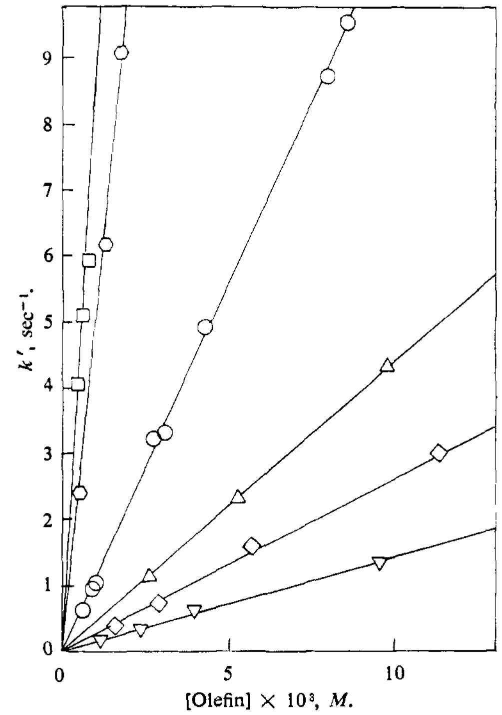

Figure 4. Dependence of k' on olefin concentration at 25°: □, 1-buten-4-ol; ○, ethylene; ○, allyl alcohol; △, 1-cyclohexen-3-ol; ◇, 1-buten-3-ol; ▽, 1-penten-3-ol.

The reported values[20] of the hydrolysis constants of Hg^{2+}, *i.e.*, $pK_1 = 3.7$ and $pK_2 = 2.6$, suggest that as the H^+ concentration is lowered from 10^{-1} to 10^{-3} M, the fraction of mercury(II) present as the unhydrolyzed Hg^{2+} ion decreases from close to 100 to 60% while the fraction of $HgOH^+$ increases from 0.1 to about 10% and the fraction of $Hg(OH)_2$ from ~0 to about 30%. The near constancy of the rates over this range implies that the reactivities of $Hg(OH)^+$ and $Hg(OH)_2$ are comparable with, and certainly not much greater than, that of Hg^{2+}. This conclusion is somewhat surprising and should be treated with some reservations in view of the possibility that the hydrolysis constants used need to be corrected for ionic strength.

Salt Effects. The effect of ionic strength (increased by addition of $NaClO_4$) on the rate of hydroxymercuration of *cis*-2-butene-1,4-diol was determined and the results are reported in Table IV. The increase in rate with increasing $NaClO_4$ concentration parallels very closely that observed for the mercuration of benzene[21] and attributed to the effect of decreasing water activity and to the accompanying increase in activity (due to "dehydration") of the metal ion. Similar salt effects have also been reported for the oxidation of olefins by thallium(III).[7,8]

Reactions with Mercurous Ion. Hydroxymercuration of olefins can also be effected by reaction with mercurous ion, *i.e.*

$$Hg_2^{2+} + {>}C{=}C{<} + H_2O \longrightarrow [Hg{>}C{-}C{<}OH]^+ + H^+ + Hg(l) \quad (7)$$

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(19) A. Brook, R. Donovan, and G. F. Wright, *Can. J. Chem.*, **31**, 536 (1953).

(20) S. Hietanen and L. G. Sillén, *Acta Chem. Scand.*, **5**, 747 (1952). The values of pK_a reported in this paper were determined at an ionic strength of 0.5 and it is possible that their correction to the lower ionic strength (0.1) used by us would result in some modification of our conclusions based on them.

(21) C. Perrin and F. H. Westheimer, *J. Am. Chem. Soc.*, **85**, 2773 (1963).

Table II. Summary of Rate Constants

Olefin	Temp, °C	k, M^{-1} sec$^{-1\,a}$
Ethylene	11	2.2×10^3
	20	4.0×10^3
	25	5.1×10^3
	32	7.6×10^3
	37	9.8×10^3
Propylene	25	$(1 \pm 0.2) \times 10^{5\,b}$
1-Butene	25	$(8 \pm 2) \times 10^{4\,b}$
Isobutene	25	$>10^{6\,c}$
cis-2-Butene	18	3.9×10^3
	25	5.8×10^3
	32	8.8×10^3
	37	12×10^3
trans-2-Butene	18	0.9×10^3
	25	1.7×10^3
	32	2.5×10^3
	37	3.3×10^3
Cyclohexene	25	$(5 \pm 1) \times 10^3$
Allyl alcohol	4	2.4×10^2
	11	4.3×10^2
	18	6.5×10^2
	25	11.2×10^2
	32	18×10^2
2-Methyl allyl alcohol	25	$(3 \pm 2) \times 10^4$
1-Buten-3-ol	4	0.54×10^2
	11	0.73×10^2
	18	1.3×10^2
	25	2.6×10^2
	25	$2.8 \times 10^{2\,d}$
	32	5.3×10^2
1-Buten-4-ol	4	2.4×10^3
	11	3.6×10^3
	18	5.6×10^3
	25	8.4×10^3
	32	11×10^3
1-Penten-3-ol	3	0.30×10^2
	11	0.52×10^2
	18	0.96×10^2
	25	1.4×10^2
	25	$1.5 \times 10^{2\,d}$
1-Penten-4-ol	3	1.4×10^3
	11	2.3×10^3
	18	3.7×10^3
	25	6.1×10^3
	32	9.6×10^3
1-Penten-5-ol	25	$>10^{6\,c}$
1-Hexen-6-ol	25	$\sim 1 \times 10^{5\,b}$
1-Cyclohexen-3-ol	3	0.86×10^2
	11	1.6×10^2
	18	2.7×10^2
	25	4.3×10^2
cis-2-Buten-1-ol	25	$(4.4 \pm 0.8) \times 10^{2\,e}$
trans-2-Buten-1-ol	25	$(2.0 \pm 0.4) \times 10^{2\,e}$
cis-2-Butene-1,4-diol	25	12
	25	13^d
	25	11.5^f
Allyl chloride	25	11^d
Allyl cyanide	25	4.3^d

[a] Rate constants measured in solutions containing 0.01 M $HClO_4$ unless otherwise stated. Ionic strength maintained at 0.10 with $NaClO_4$. [b] Low precision due to very fast reaction. [c] Too fast to measure; lower limit based on assumption of second-order kinetics. [d] Rate based on H^+ formation using cresol red indicator. [e] Derived from rate measurements on a series of mixtures of *cis*- and *trans*-2-buten-1-ol of known compostion. [f] In D_2O.

Table III. Activation Parameters

Olefin	$\Delta H^{\ddagger}$ ($\pm$ 0.5), kcal/mole	$\Delta S^{\ddagger}$ ($\pm$ 1), eu
Ethylene	9.2	−10
trans-2-Butene	12.0	−3
cis-2-Butene	9.6	−9
Allyl alcohol	10.7	−8
1-Buten-3-ol	13.5	−5
1-Buten-4-ol	8.7	−11
1-Penten-3-ol	11.7	−9
1-Penten-4-ol	10.7	−5
1-Cyclohexen-3-ol	11.6	−7
cis-2-Butene-1,4-diol	13.5	−11

Table IV. Salt Effects on the Rates of Hydroxymercuration of *cis*-2-Butene-1,4-diol at 25°, 0.50 M $HClO_4$

$NaClO_4$, M	k, M^{-1} sec^{-1}
0.090	12^a
1.0	32
2.0	79
3.0	1.3×10^2
4.0	2.9×10^2
5.5	1.3×10^3

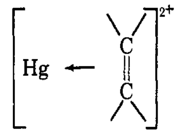
[a] 0.01 M $HClO_4$.

The rates of the reactions of 1-buten-3-ol and *cis*-2-butene-1,4-diol with Hg_2^{2-} were determined in solutions of mercurous perchlorate equilibrated with metallic mercury. The apparent rate constant (defined by rate/$[Hg_2^{2+}][>C{=}C<]$), at 25° was found in each case to be close to 0.006k (where k is the corresponding rate constant for reaction with Hg_2^{2+}). The observed rate is thus quantitatively accounted for by reaction of the olefin with the Hg^{2+} in equilibrium with Hg_2^{2+} through the rapidly established dismutation equilibrium

$$Hg_2^{2+} \rightleftharpoons Hg^{2+} + Hg(l) \qquad (8)$$

for which K_{eq} (= $[Hg^{2+}]/[Hg_2^{2+}]$) = 0.006.[22] The contribution from a direct reaction between the olefin and Hg_2^{2+} thus appears to be negligible.

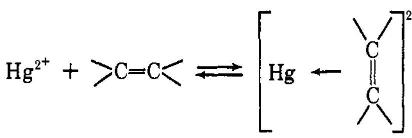
Mechanism of the Reaction. Evidence Concerning a Mercurinium Ion Intermediate. The simplest interpretation of the kinetic behavior described above is in terms of a mechanism involving a bimolecular rate-determining reaction between Hg^{2+} and the olefin. The possibility of a mechanism involving a mercurinium ion (*i.e.*, mercury(II)–olefin π complex) intermediate (III), which several earlier workers have proposed,[5,10]



III

is not excluded but the results do place certain restrictions upon the role which can be assigned to such an intermediate. In particular the following limiting possibilities merit consideration.

(1) Formation of the mercurinium ion, *i.e.*



(9)

is the rate-determining step. This is not inconsistent with the observed kinetics but is considered unlikely in the light of the very high rates (approaching diffusion controlled) of formation of other mercury(II) com-

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(22) W. L. Latimer, "Oxidation Potentials," 2nd ed, Prentice-Hall, Inc., Englewood Cliffs, N. J., 1952.

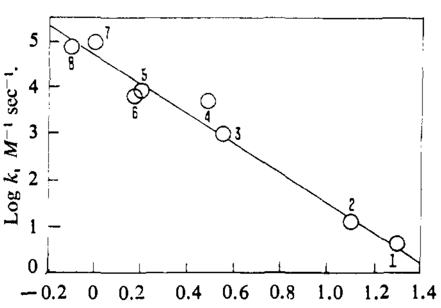


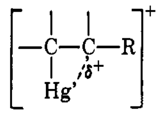
Figure 5. Correlation of substituent effects with Taft's σ*: 1, allyl cyanide; 2, allyl chloride; 3, allyl alcohol; 4, ethylene; 5, 1-buten-4-ol; 6, 1-penten-4-ol; 7, propene; 8, 1-butene.

plexes[23] and the high rates of formation of olefin complexes of other d^{10} metal ions, *e.g.*, Ag^+.

(2) Formation of the mercurinium ion (reaction 9) is a rapid preequilibrium, followed by a rate-determining rearrangement, or reaction with water, to yield the hydroxymercuration product. Such a preequilibrium would be expected to lead, ultimately, to a fall-off from first-order dependence on the olefin concentration (Michaelis–Menten-type kinetics) as the olefin concentration is increased to the point that the fraction of mercury(II) present as the olefin complex becomes appreciable. Failure to detect such a fall-off from first-order dependence on the olefin concentration in any of the reactions examined (as illustrated by the results in Figure 4) does not, of course, preclude such a preequilibrium, but it does permit upper limits to be placed on the preequilibrium formation constants for the mercury–olefin intermediates. Typical values of such upper limits, estimated in this way, for various olefins are: ethylene, 1×10^2 M^{-1}; *trans*-2-butene, 1×10^2 M^{-1}; *cis*-2-butene, 2×10^2 M^{-1}; allyl alcohol, 10 M^{-1}; 1-buten-3-ol, 10 M^{-1}; 1-buten-4-ol, 70 M^{-1}; 1-penten-3-ol, 2 M^{-1}; 1-cyclohexen-3-ol, 10 M^{-1}; *cis*-2-butene-1,4-diol, 0.5 M^{-1}; allyl cyanide, 4 M^{-1}; cyclohexene, $\sim 2 \times 10^2$ M^{-1}. Formation constants consistent with these upper limits do not appear to be unreasonable for mercury(II)–olefin complexes, since the known formation constants[24] of the silver(I) complexes of several of the olefins are of the same order (*e.g.*, 85 M^{-1} for ethylene; 29 M^{-1} for *trans*-2-butene; 72 M^{-1} for *cis*-2-butene; 14 M^{-1} for allyl alcohol, etc.). The upper limit of 2×10^2 M^{-1} for the mercury(II)–cyclohexene complex is, however, inconsistent with the value of 2.2×10^4 M^{-1} for the formation constant of the corresponding mercurinium ion, reported by Lucas, *et al.*[10] The origin of this apparent contradiction is unclear and merits further investigation.

Substituent Effects on the Rate of Hydroxymercuration. Evidence Concerning the Nature of the Transition State. As expected for an electrophilic addition, the rate of oxymercuration is increased by electron-donating substituents (alkyl groups) and decreased by electron-withdrawing substituents (–OH, –Cl, –CN). For the olefins to which this treatment can be applied, an excellent correlation is found on plotting log $k_{RCH=CH_2}$ *vs.* Taft's[25] σ* for R (Figure 5). The values of σ* are taken from Taft's paper,[25] except those for R = $-CH_2CH_2OH$ and $-CH_2CH(OH)CH_3$, which were calculated by Taft's method using the relation $\sigma^*(R-)/\sigma^*(RCH_2-) = 2.8$.

The plot of log *k vs.* σ* in Figure 5 yields the value $\rho^* = -3.3$, implying a high degree of positive charge localization (approaching carbonium ion character), in the transition state, on the carbon atom adjacent to the substituent R, *i.e.*



A similar correlation between log k'' and σ* ($\rho^* = -2.77$) has been reported by Kreevoy, *et al.*,[26] for the acid-induced deoxymercuration of two series of oxymercurials, $RCH(OH)CH_2HgI$ and $RCH(OCH_3)CH_2HgI$. The conclusion reached in the latter case, namely that the transition state does not resemble the protonated starting state, but rather a configuration intermediate between the initial state, the olefin–mercuric monoiodide and the carbonium ion, is not inconsistent with our own conclusion concerning the mechanism of hydroxymercuration, although it should be recognized that because of the presence of iodide in the deoxymercuration case, the two reactions being compared are not strictly the reverse of each other. Arguments analogous to those developed by Bartlett and Sargent[27] also point to a transition state in which the positive change is localized to a large degree on one of the carbon atoms rather than distributed over both as in the mercurinium ion (III). On the basis of analogous observations concerning the effect of substituents on the rate of the oxidation of olefins by thallium(III), for which a mechanism involving a rate-determining oxythallation step was proposed, Henry[7] has reached similar conclusions, favoring a transition state with considerable carbonium ion character. On the other hand, a completely free (open) carbonium ion intermediate in oxymercuration appears to be ruled out by the failure to observe *cis–trans* isomerization during the successive oxymercuration–deoxymercuration of internal olefins such as *cis*- or *trans*-butene[16] or *cis*-stilbene.[28] Failure to observe the rearrangement associated with the norbornyl cation, during the oxymercuration of norbornene,[5,29] also argues against a free carbonium ion mechanism in the latter case.

The exceptionally high rate ($k > 10^6$ M^{-1} sec^{-1}) of the oxymercuration of 1-penten-5-ol (reaction 2), which is out of line with the other rates, presumably reflects a neighboring group participation of the 5-hydroxy substituent, which is capable of stabilizing the carbonium ionlike transition state by interaction through a five-membered ring approaching that of product I. Such neighboring group participation, as reflected in the formation of cyclic products, indeed is common among

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[23] M. Eigen and R. G. Wilkins, Advances in Chemistry Series, No. 49, American Chemical Society, Washington, D. C., 1965, p 55.

[24] L. G. Sillén and A. E. Martell, "Stability Constants," Special Publication No. 17, The Chemical Society, London, England, 1964.

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[26] L. L. Schaleger, M. A. Turner, T. C. Chamberlin, and M. M. Kreevoy, *J. Org. Chem.*, 27, 3421 (1962).

[27] P. D. Bartlett and G. D. Sargent, *J. Am. Chem. Soc.*, **87**, 1297 (1965).

[28] M. M. Kreevoy, N. Takashina, and L. L. Schaleger, Abstracts, 137th National Meeting of American Chemical Society, Cleveland, Ohio, April 1960.

[29] H. C. Brown, J. H. Kawakami, and S. Ikegami, *J. Am. Chem. Soc.*, **89**, 1525 (1967).

oxymercuration reactions.[18,30] Analogous rate enhancements due to neighboring group effects have also been observed by Peterson[31] in other electrophilic additions (*e.g.*, of trifluoroacetic acid) to olefins. Not unexpectedly, and in line with similar observations for other reactions,[31] the corresponding effect is much less marked in the oxymercuration of 1-hexen-6-ol which leads to a six-membered ring (reaction 3).

Acknowledgment. We are grateful to Professor M. M. Kreevoy for helpful comments.

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A Theoretical Interpretation of the Signs and Magnitudes of Some Phosphorus-31 and Silicon-29 Nuclear Spin Coupling Constants

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Abstract: An attempt has been made to explain the observed pattern of signs and magnitudes of the ^{31}P–^{1}H, ^{31}P–^{19}F, ^{31}P–^{31}P, ^{29}Si–^{1}H, and ^{29}Si–^{19}F nuclear spin coupling constants on the basis of the Pople and Santry expression for the contact term. To do this it was necessary to perform LCAO–MO calculations on the following model compounds: PH_3, PH_4^+, PF_3, P_2, SiH_4, and SiF_4. Both extended Hückel and self-consistent field calculations were employed. With the exception of SiF_4 a satisfactory agreement between the observed and calculated signs was observed. The calculated magnitudes of the coupling constants also correlate with the observed values but are lower by a factor of between 2 and 3.

Recently we have had occasion to determine the relative signs and magnitudes of the nuclear spin coupling constants in a number of compounds involving directly bonded P–H, P–F, and P–P linkages.[2] In this study it was shown that the signs of the ^{31}P–^{1}H, ^{31}P–^{19}F, and ^{31}P–^{31}P coupling constants are positive, negative, and negative, respectively. Earlier Danyluk had demonstrated that the ^{29}Si–^{1}H and ^{29}Si–^{19}F coupling constants are opposite in sign.[3] In the present paper we attempt to gain a theoretical understanding of the pattern of signs and magnitudes which has been observed for the above couplings.

The interactions which lead to spin–spin coupling in liquids were first formulated by Ramsey[4] in terms of a contact (Fermi) mechanism, a spin-orbital mechanism, and a spin-polarization mechanism. Later McConnell[5] showed that Ramsey's formulas could be applied to large molecules if LCAO molecular orbitals were used in conjunction with the "average excitation energy" approximation. By the latter one means that all triplet states interacting with the ground state are replaced by a suitable average value. This approach, which also eliminates triplet-state wave functions, produced useful formulas for calculating various coupling constants, but necessarily could predict only positive signs. The next significant step was taken by Pople and Santry[6] who avoided the use of the "average excitation energy" approximation and were thus able to predict a satisfactory pattern for the signs and magnitudes of the coupling constants between various directly bonded atoms up to fluorine.

In the present paper we extend the Pople and Santry approach to various couplings involving phosphorus and silicon. The majority of the experimental results are discussed in relation to the contact term. However, we have attempted to estimate the orbital and spin-dipolar contributions in those couplings which do not involve hydrogen.

The molecular orbital expression for the contact contribution to the spin–spin coupling constant between directly bonded nuclei A and B is given by[6]

$$J_{AB} = \frac{-64}{9}\beta^2\gamma_A\gamma_B h \sum_i^{\text{occ}} \sum_j^{\text{unocc}} ({}^3\Delta E_{i\rightarrow j})^{-1} \times (\psi_i|\delta(r_A)|\psi_j)(\psi_j|\delta(r_B)|\psi_i) \quad (1)$$

where β is the Bohr magneton, γ is the magnetogyric ratio, and the terms in the summation relate to the interaction of the triplet excited states with the ground state evaluated at the A and B nuclei. In the LCAO

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(1) (a) University of Texas; (b) Union Carbide Predoctoral Fellow, University of Texas; (c) Jet Propulsion Laboratory.

(2) S. L. Manatt, D. D. Elleman, A. H. Cowley, and A. B. Burg, *J. Am. Chem. Soc.*, **89**, 4544 (1967).

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(6) J. A. Pople and D. P. Santry, *Mol. Phys.*, **8**, 1 (1964).