It is apparent that these values of the time delay are averages of a particular sort. Nevertheless, the values seem to be a sensible order of magnitude. It is interesting to note that the effect of increasing the value of s from 18 to 26 increases $\bar{l}_0$ by a factor of 150. But decreasing s from 18 to 11 (and E_0 to 48.6 kcal, for some molecule with *fewer* atoms) decreases $\bar{l}_0$ by a factor of 1040, *i.e.*, to 5.3×10^{-6} sec. $\bar{l}_0$ is a weak function only of the temperature, decreasing by a factor of less than 5 for a temperature increase of 70° for cyclobutane. $\bar{l}$ is, of course, always smaller than τ, but is approaching τ as the pressure is increased.

We reemphasize that the times calculated by this theory represent an average lifetime for active molecules which actually react. The lifetimes of activated molecules which are deactivated by collision are not counted.

Acknowledgment. We wish to thank the Atomic Energy Commission for support.

Aqueous Solubilities of Potassium, Rubidium, and Cesium Perchlorates

William B. Guenther

Contribution from the Department of Chemistry, University of the South, Sewanee, Tennessee 37375. *Received June 2, 1969*

Abstract: The solubilities of $KClO_4$, $RbClO_4$, and $CsClO_4$ at 25° have been determined in the presence of some uniunivalent strong electrolytes varying the ionic strength from 0.068 to 0.46 *M*. Contrary to earlier indications, close agreement with simple Debye-Hückel theory was found with $RbClO_4$ and $CsClO_4$ generally, and with $KClO_4$ at lower ionic strengths and with some of the added electrolytes. A water solubility of 0.0683 ± 0.0003 *M* at 25° for $RbClO_4$ was found, resolving lack of agreement among previously reported results. The negative logarithms of the thermodynamic solubility product constants derived from the data are: $KClO_4$, 1.944; $RbClO_4$, 2.542; and $CsClO_4$, 2.380.

The low coordinating and associating tendencies of the ions in potassium, rubidium, and cesium perchlorates in water make them ideal for study of interionic effects on their solubility equilibria. The ionic strengths available extend down to 0.068 *M* for the least soluble, $RbClO_4$. This study lies partly in the region about 0.05–0.2 *M* ionic strength in which deviations from the Debye–Hückel relation in eq 1 often begin to appear as added electrolyte concentration increases. In eq 1

$$\log \gamma_\pm = -0.509\sqrt{I}/(1 + A\sqrt{I}) \qquad (1)$$

I is ionic strength and $\gamma_\pm$ is the mean molar[1] ionic activity coefficient. Ion pairing could produce solubilities higher than in mixtures following eq 1. Only uniunivalent electrolytes are considered here and the factor A is not significantly different from unity for the ions K^+, Rb^+, Cs^+, Cl^-, and ClO_4^-,[2] for I near 0.1 *M*. If we take the thermodynamic solubility constant[3] to be $K_{s_0}\gamma_\pm^2 = K_{s_0}^0$ and $K_{s_0} = [M^+][ClO_4^-]$, we get from this and eq 1

$$\log K_{s_0} = \log K_{s_0}^0 + 1.018\sqrt{I}/(1 + \sqrt{I}) \qquad (2)$$

Molarity at 25° is used throughout this paper.

Several studies of $KClO_4$ solutions appeared many years ago.[4–6] It is the most soluble of the three perchlorates, 0.148 *M*, so that rather high ionic strengths were reached in these studies. The last one[6] implied that specific ion effects are so great that no clear limiting behavior such as given by eq 2 is followed. Of course, the form of eq 2 was not used at that time. For $RbClO_4$ and $CsClO_4$, only pure water solubilities had been reported.[4,7] The present study was made to find out how the solubilities of the last two vary with ionic strength, to reexamine the behavior of $KClO_4$, and to resolve contradictions among published values for the $RbClO_4$ solubility and thermodynamic data for the Rb^+ ion.

Earlier determinations of solubilities were made by evaporation and weighing of remaining nonvolatile solutes. In the present work, tetraphenylborate precipitation methods were used. Their specificity and reliability make the results reliable to within a few parts per thousand of the solubility molarity.

Experimental Section

Materials. $KClO_4$ was reagent grade, recrystallized twice from water. CsCl was Fisher reagent certified 99.9%. $CsClO_4$ was prepared from the CsCl or from 99.9% Cs_2CO_3 (K and K Laboratories, Inc., Plainview, N. Y.) by adding excess $HClO_4$ and recrystallizing the solid twice from water. $RbClO_4$ was obtained from G. F. Smith Co. who state that it is normally 0.1–0.3% $KClO_4$, but may reach 1% $KClO_4$. The various high results previously reported

---

[1] J. N. Butler, "Ionic Equilibrium," Addison-Wesley Publishing Co., Reading, Mass., 1964, p 433, gives reasons for the value 0.509 for *M* units.

[2] J. Kielland, *J. Am. Chem. Soc.*, **59**, 1675 (1937).

[3] K_{s_0} is used here for the traditional K_{sp} in accordance with recent international usage. See ref 1 and "Stability Constants," Special Publication No. 17, The Chemical Society, London, 1964.

[4] A summary of solubilities and references to earlier papers are found in A. Seidell, "Solubilities of Inorganic and Metal Organic Compounds," 4th ed, W. Linke, Ed., The American Chemical Society, Washington, D. C.: Vol. 1, 1958; Vol. 2, 1965.

[5] A. A. Noyes and C. R. Boggs, *J. Am. Chem. Soc.*, 33, 1650 (1911).

[6] R. M. Bozorth, *ibid.*, **45**, 2653 (1923).

[7] R. Flatt and A. Jordan, *Bull. Soc. Chim. Fr.*, **47**, 246 (1930); *Helv. Chim. Acta*, **16**, 37 (1933).

Table I

Sample	Apparent % Rb
Crystals from recrystallization liquor	46.46
Reagent $RbClO_4$ as received	46.42
After two recrystallizations from water	46.30
After four recrystallizations from water	46.24
Calculated from the formula	46.22

for $RbClO_4$ solubility made it desirable to test the material for purity. The rubidium content of the material which had been dried at 120° for 1 hr approached the expected value after several recrystallizations from water as shown by the gravimetric results in Table I.

The four-times recrystallized material was used throughout this work. RbCl needed for one solution was prepared by heating the purified $RbClO_4$ and melting the product RbCl, mp 715°. The solution made by weight of this material was checked by titration with standard $AgNO_3$. Other solids were reagent grade and their solutions were made from dried samples. Lithium perchlorate and some of the other solutions had their concentrations checked through ion exchange.

Fisher certified grade sodium tetraphenylborate was used. Clarification by $Al(OH)_3$ treatment did not seem required on this grade material. The solution for gravimetric determination was made just before use and filtered.

Tetraphenylborate Methods. A volumetric back-titration was used for a few mixtures as noted in Table II. A published method was followed except that titian yellow was the indicator.[8] Agreement with gravimetric results was within 5 ppt (parts per thousand) but the gravimetric method was considered more reliable and used for most of the work. The main features of the method in ref 9 were followed. For potassium determination, precipitation was made from 0.1 *M* HCl solution at room temperature, and the mixture was cooled to about 5° before filtration. Using 5–15 ml of ice water for washing the solid, results consistently 5 ppt low were obtained. This correction was added to all determinations of K. Appelman[10] also found need for such a factor. He used 7.5 ppt on a smaller sample. The much lower solubility Rb and Cs tetraphenylborates provided results within ±2 ppt on known samples giving about 200 mg of precipitate. Check determinations with pure KCl, $RbClO_4$, and CsCl were made at intervals throughout this work. We believe that unknown sample determinations can be relied upon to within ±3 ppt. In the cases of Rb and Cs, very fine precipitates of tetraphenylborates may form. To improve filterability, the samples were made close to 0.1 *M* in HCl and warmed to about 50°, and then the NaTPB, 10–20% in excess, in 40 ml of water was added dropwise with constant stirring. After cooling to about 18°, the product was filtered through weighed *fine* grade porcelain filter crucibles stated to have average pore diameter of 5 μ. The crucibles were cleaned between uses with hot water, acetone, and concentrated HNO_3. A set of five, used through a series of 11 determinations in each, lost gradually 2 mg in their empty weight under standardized conditions. A single-pan balance, with class S weights checked against an NBS certified set, was used.

Volumetric ware was calibrated, and no pipet smaller than 20 ml was used in taking aliquots. Bath thermometers were checked in ice and at the Na_2SO_4 point. Temperature was controlled within less than ±0.1°. This keeps the solubility uncertainty under ±0.4% for each of the perchlorates in water.[4]

Equilibration. Solubility equilibrium was approached from higher and lower temperatures. Some samples of $RbClO_4$ stirred less than 24 hr were not yet at equilibrium. Most mixtures remained in the 25° bath for 2 weeks with a minimum total stirring time of 48 hr. Teflon-coated magnetic stirring bars were used.

Results

The data and calculated results appear in Table II. Points included from earlier reports are noted under $KClO_4$. The five columns contain: (1) the aqueous medium excluding the dissolved $MClO_4$, (2) the solubility of $MClO_4$ found, (3) the final ionic strength of the solution, (4) the negative logarithm of the molar solubility product in the given medium, (5) the negative logarithm of the $K_{s_0}{}^0$ as calculated from eq 2. This helps point out the specific effects in the last four cases under $KClO_4$.

Table II. Solubilities at 25° (Molarity)

Medium	$MClO_4$ dissolved	I	$-$Log K_{s_0}	$-$Log $K_{s_0}{}^0$ (calcd)
		A. $KClO_4$		
H_2O	0.1476	0.1476	1.6618	1.9444
0.0506 KCl	0.1277	0.1783	1.6425	1.9447
0.0497 KCl[a]	0.1282	0.1779	1.6419	1.9438
0.0967 KCl[b]	0.1117	0.2084	1.6330	1.9521
0.0993 KCl[a]	0.1123	0.2116	1.6241	1.9449
0.2944 KCl[b]	0.0745	0.3689	1.5611	1.9458
0.1004 $NaClO_4$[b]	0.1098	0.2102	1.6368	1.9568
0.3038 $NaClO_4$[b]	0.0739	0.3777	1.5542	1.9427
0.0925 $HClO_4$	0.1111	0.2036	1.6455	1.9620
0.0504 NaCl	0.1523	0.2026	1.6345	1.9505
0.0990 NaCl[b]	0.1540	0.2530	1.6249	1.9656
0.2937 NaCl[b]	0.1626	0.4563	1.5777	1.9881
		B. $RbClO_4$		
H_2O	0.0683	0.0683	2.3307	2.5416
0.0200 $LiClO_4$	0.0602	0.0802	2.3164	2.5409
0.0492 RbCl	0.0505	0.0997	2.2981	2.5422
0.0200 NaCl[c]	0.0702	0.0902	2.3073	2.5425
0.0300 NaCl[c]	0.0708	0.1008	2.3000	2.5453
0.0400 NaCl[c]	0.0717	0.1117	2.2890	2.5445
0.05036 NaCl	0.0726	0.1229	2.2788	2.5431
0.0200 $HClO_4$[c]	0.0598	0.0798	2.321	2.546
0.0500 $HClO_4$[c]	0.0500	0.1000	2.301	2.546
0.1000 $HClO_4$[c]	0.0386	0.1386	2.272	2.548
		C. $CsClO_4$		
H_2O	0.0840	0.0840	2.1514	2.3802
0.0334 CsCl	0.0715	0.1049	2.1249	2.3739
0.0617 CsCl	0.0626	0.1243	2.1088	2.3742
0.0984 CsCl	0.0525	0.1509	2.1003	2.3851

[a] Reference 5. [b] Recalculated from molality data, ref 6. Need for estimation of densities may introduce errors up to ±5% in *M*. [c] Volumetric determinations.

Figure 1 illustrates conformity with eq 2 by showing the relation of the experimental points to a straight line of slope 1.018 constructed through the pure water solubility point for each perchlorate. In the top line for $KClO_4$, only mixtures with common ion added electrolytes are shown. The first two points are from the present work. The water solubility found here, 0.1476 ± 0.0004 *M*, agrees well with two carefully done previous studies, 0.1481[5] and 0.1475 *M* (given as 0.1491 *m*, $d = 1.0096$ g/ml).[6]

In the second line, for $CsClO_4$, CsCl was the added electrolyte. The water solubility reported here is 0.0840 ± 0.0003 *M* in agreement with 0.0842 *M* (reported as 0.0849 *m*).[7] The density of this solution was measured and agreement found with 1.010 g/ml[7] and not 1.016 g/ml reported by others.[4,11]

The third line is for $RbClO_4$. Ionic strength varied from 0.068 to 0.14 *M* without significant deviation from eq 2. The water solubility reported here is 0.0683 ± 0.0003 *M* which agrees with the 1933 value of Flatt and Jordan,[7] 0.0683 *M* (reported as 0.0688 *m*, $d = 1.006$ g/ml), but disagrees with values up to 0.072 *M* reported by others.[4,11] Since the higher value is

---

[8] R. Belcher and C. L. Wilson, "New Methods of Analytical Chemistry," Chapman and Hall Ltd., London, 2nd ed, 1964, pp 174, 177.

[9] S. Kallman in "Treatise on Analytical Chemistry," Part 2, Vol. I, I. M. Kolthoff and P. J. Elving, Ed., Interscience Publishers, New York, N. Y., 1961, pp 374, 439.

[10] E. H. Appelman, *Inorg. Chem.*, **8**, 223 (1969).

[11] H. H. Willard and G. F. Smith, *J. Am. Chem. Soc.*, **45**, 286 (1923).

widely quoted, the purification was examined as described above in the Experimental Section, and the water solubility was checked several times by three methods: evaporation and weight, and four volumetric, and two gravimetric tetraphenylborate determinations. All gave results between 0.0680 and 0.0688 *M* with no systematic differences among the methods. A solubility about 0.070 was found for the unpurified $RbClO_4$. Higher published values may stem from the presence of $KClO_4$ or from NH_4ClO_4 introduced in one method of purification described.[11]

Discussion

It seems safe to assume that association between any of the heavier alkali metal ions and perchlorate ions in dilute water solution is negligible for the purposes of this study. Some evidence for weak association with K^+ and ClO_4^- has been reported in ref 3, but a Raman spectrum study reports negative results for this pair of ions.[12] The data of the present study when plotted as $[M^+]$ *vs.* $1/[ClO_4^-]\gamma_\pm^2$ gives straight lines of zero intercept indicating no measurable association.

The high ionic strengths of the $KClO_4$ solutions might lead one to expect deviations from eq 2. Bozorth[6] found different specific behavior for added electrolytes in $KClO_4$ solutions when the salts were NaCl, $NaNO_3$, KNO_3, K_2SO_4, Na_2SO_4, $BaCl_2$, and $Ba(NO_3)_2$. But, KCl and $NaClO_4$ gave the limiting eq 2 behavior as pointed out above. The NaCl data approach the eq 2 line as *I* decreases in Bozorth's data and in one lower *I* point which we did to test this agreement, the one at 0.0504 *M* NaCl. Thus, it seems that simple Debye–Hückel behavior, eq 1 or 2, correctly describes even this rather soluble material at ionic strengths below about 0.3 *M* and should be adequate for calculation of the thermodynamic constant $K_{s_0}{}^0$.

With $RbClO_4$ and $CsClO_4$, all the solutions of this study were below ionic strength 0.15 *M* and eq 2 was obeyed within experimental error for the electrolytes used. The major portion of our experimental work was spent on $RbClO_4$, the least soluble of the three perchlorates. The four points obtained with $CsClO_4$ were enough to establish the plausibility that it is quite similar in behavior to $RbClO_4$. However, one should not rule out the possibility of different specific effects of added electrolytes not tested. It should be clear Bozorth's varied specific ion effects with the 1:1 electrolytes, KNO_3, $NaNO_3$, and NaCl occurred at his relatively high ionic strengths, above 0.25 *M*, in the $KClO_4$ solubility study. We plan further work to follow up our preliminary indications that H^+, Li^+, and NO_3^- ions produce deviations from eq 2 in $RbClO_4$ and $CsClO_4$ solubility above $I = 0.15$ *M*.

Values for thermodynamic solubility constants can be obtained from eq 2, or from the extrapolation in Figure 1. We report for $-\log k_{s_0}{}^0$: $KClO_4$ 1.944, $RbClO_4$ 2.542, and $CsClO_4$ 2.380 at 25°. The $\Delta G°$, from $-RT \ln K_{s_0}{}^0$, in each case can be combined with "best" values of $\Delta H_\infty{}°$,[13] standard heats of solution, and standard entropies for the solids and for the ClO_4^- ion to obtain standard ionic entropies: K^+ 24.6, Rb^+ 28.7, and Cs^+ 31.9 eu. These $S°$ values for K^+ and Cs^+ agree satisfactorily with those listed in "Selected Values of Chemical Thermodynamic Properties" (SVCTP).[14] However, the listed value of 29.7 eu[14] for Rb^+ does not agree with any reasonable solubility of $RbClO_4$. It seems that SVCTP has miscopied the recommended value of 28.7 in its source reference.[15] This is also the value of previous reports. The standard ionic free energy of Rb^+ which conforms to this entropy, 28.7 eu, and to the $\Delta G°$ of solution confirmed here is −67.15 kcal/mole, rather than the −67.45 kcal/mole listed in SVCTP.[14] The slight difference between *M* and *m* scales when extrapolated to zero ionic strength at 25° is less than the experimental uncertainty in $K_{s_0}{}^0$.

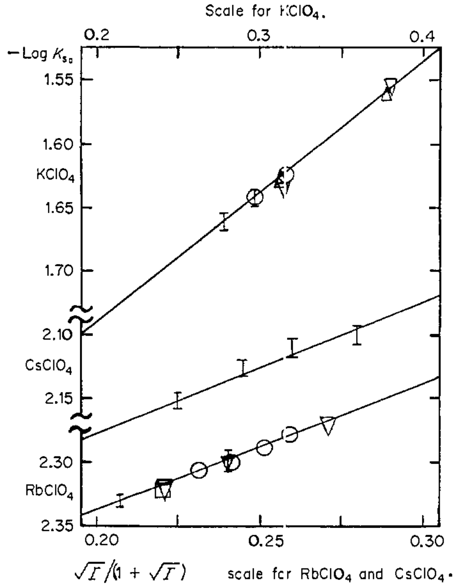

Figure 1. First points, pure water solubility. Added electrolytes in each case were: $KClO_4$—circles[5] and triangles,[6] KCl; inverted triangles,[6] $NaClO_4$ ($CsClO_4$: CsCl); for $RbClO_4$—square, $LiClO_4$; circles, NaCl; triangles, $HClO_4$; I, RbCl.

Other studies on $KClO_4$ have been reported.[4] They had different and less accurate purposes and will not be discussed here.

A study of the solubility of rubidium iodate in KNO_3 and in HNO_3 solutions has been made.[16] Equation 2 was followed from the pure water solubility, 0.0919 *M* up to $I = 0.25$ in the presence of KNO_3. Then deviation increased gradually up to the maximum, 0.6 *M*, used. Lack of agreement with the HNO_3 solutions may be ascribed, in part, to the IO_3^- ion which is a base, and is capable of both oxidation and reduction at higher acidities. Unfortunately, heat of solution and entropy values for $RbIO_3$ are not available so that a check on the $S°$ of Rb^+ cannot be made with this solubility data.

---

(12) M. M. Jones, E. A. Jones, D. F. Harmon, and R. T. Semmes, *J. Am. Chem. Soc.*, 83, 2038 (1961).

(13) V. B. Parker, "Thermal Properties of Aqueous Uni-univalent Electrolytes," National Bureau of Standards Reference Data Series, National Bureau of Standards, U. S. Government Printing Office, Washington, D. C., April 1, 1965.

(14) "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards Circular 500, U. S. Government Printing Office, Washington, D. C., 1950.

(15) K. K. Kelley, "Contributions to the Data on Theoretical Metallurgy. IX. The Entropies of Inorganic Substances," U. S. Bureau of Mines Bulletin 434, U. S. Government Printing Office, Washington, D. C., 1941.

(16) W. D. Larsen and J. J. Renier, *J. Am. Chem. Soc.*, **74**, 3184 (1952).

It seems that alkali metal compounds of low solubility with large neutral anions should follow Debye–Hückel eq 1 and should provide a simple method of investigating specific and mixed ion effects at ionic strengths in the range 0.1–0.3 M.[17]

Acknowledgment. The volumetric results for $RbClO_4$ were obtained by Jonathan Fletcher supported by an undergraduate research participation grant from the National Science Foundation in the summer of 1967.

(17) A paper on the solubility of $RbClO_4$ and $CsClO_4$ in aqueous $HClO_4$ by S. M. Arkhipov and N. I. Kashina, *Z. Neorg. Khim.*, **14**, 1114 (1969), was listed in *Chemical Titles* in May 1969. It was not available at the time this paper was written.

Thermal Decomposition of 1,1,3,3-Tetramethylcyclobutane[1,2]

Thomas A. Babcock

Contribution from the Department of Chemistry, University of Rochester, Rochester, New York 14627. Received May 5, 1969

Abstract: The thermal decomposition of 1,1,3,3-tetramethylcyclobutane has been studied in the pressure region 7.65–42.8 mm at 435.7° and over the temperature range 415–455°. The reaction yielding two molecules of isobutylene as the primary product is a first-order process which occurs homogeneously, and the rate does not seem to be affected significantly by the addition of nitric oxide or propylene. Experiments near 10-mm pressure in the 40° temperature range indicate that the activation energy for the decomposition is 64.8 ± 0.3 kcal/mole. The first-order rate constant may be expressed as $k = (1.74 \pm 0.02) \times 10^{16} \exp(-64{,}800/RT)\ \mathrm{sec}^{-1}$. Occurring simultaneously with the decomposition, there is a slow structural isomerization to yield 2,4,4-trimethyl-1-pentene. When the results of this study are compared with previous data for the decomposition of cyclobutane, it is found that 1,1,3,3-tetramethylcyclobutane reacts about 0.83 times as fast as cyclobutane.

In recent years much interesting information concerning the homogeneous, vapor-phase pyrolyses of alkyl-substituted small-ring hydrocarbon compounds has been obtained. From the results of earlier studies of thermal decompositions of alkyl-substituted cyclobutanes,[3-6] it has been possible to make some comparison of the effect of the substitution upon the kinetics of the first-order reaction such as for the monoalkylcyclobutanes.

(1)

The activation energies and preexponential factors for the reactions of alkylcyclobutanes are not far apart, but a comparison of the calculated first-order rate constants taken at 450° indicates definite differences in the influence of the alkyl groups. For the series (cyclobutane, methylcyclobutane, and 1,1-dimethylcyclobutane) the relative rates are 1.0:1.5:3.4. This observation seems to be in good agreement with the results observed in the cyclopropane series where the addition of each methyl group results in approximately a doubling of the rate. In order to study further the effects of methylation on the decomposition of the cyclobutane ring, it was of interest to investigate the kinetic behavior of 1,1,3,3-tetramethylcyclobutane.

Experimental Section

Materials. 1,1,3,3-Tetramethylcyclobutane was prepared by a Wolff–Kishner reduction of 2,2,4,4-tetramethylcyclobutane-1,3-dione according to the procedure suggested by Herzog and Buchman[7] and with modifications suggested by Lautenschlaeger and Wright.[8] The disemicarbazone was formed from the diketone by a method described by Wedekind and Weisswange.[9] The 1,1,3,3-tetramethylcyclobutane which was formed upon the reduction of the disemicarbazone was fractionated in a spinning-band column at a reflux ratio of about 15:1. The fraction obtained in the range 85–86° at 748 mm appeared to contain the desired compound. The literature reports that the pure compound boils at 86–87° at 748 mm.[7] For the kinetic study this fraction was further purified on a Perkin-Elmer Model 154D gas chromatograph with a 2-m R-X column (13% by weight UCON LB-550-X oil on a GC-22 base supplied by the Coast Engineering Laboratory) heated to 78°. The purity was found to be at least 99.8% on eight different gas chromatographic columns.

The refractive index $n^{25}\mathrm{D}$ of the purified sample was found to be 1.3915 (lit.[7] $n^{25}\mathrm{D}$ 1.3930). Duplicate carbon–hydrogen analyses yielded the following percentages: C, 85.7, 85.7; H, 14.4, 14.3 (theoretical, C, 85.63; H, 14.37). The synthesized compound gave a nuclear magnetic resonance spectrum on a Varian A-60 instrument and a mass spectrometric fragmentation pattern at 70 eV which would be expected for 1,1,3,3-tetramethylcyclobutane. A gas-phase infrared spectrum of a 60-mm sample in a cell with a 7.5-cm path length was determined on a Perkin-Elmer Model 421 spectrophotometer. Major absorption peaks were observed at 1155, 1265–1270, 1365–1372, 1430–1465, and 2860–2970 cm^{-1} with smaller absorptions at 950, 1200, 1650–1720, 2645, 2720, and 3240 cm^{-1}. This spectrum agrees with what Lautenschlaeger and Wright observed for 1,1,3,3-tetramethylcyclobutane.

Isobutylene (99.8%, Matheson), propylene (99.9%, Phillips), and 2,4,4-trimethyl-1-pentene (99.9%, Chemical Samples) were purified on the gas chromatograph prior to analytical use. Nitric oxide (99.0%, Matheson) was subjected to low-temperature distillation from trap to trap. All samples were degassed and dried before use.

---

(1) This work was supported in part by a grant from the National Science Foundation.

(2) Abstracted in part from the M. S. thesis submitted to the University of Rochester by T. A. Babcock, 1968.

(3) S. M. E. Kellner and W. D. Walter, *J. Phys. Chem.*, **65**, 466 (1961); in this paper references to earlier studies are given.

(4) M. Zupan and W. D. Walters, *ibid.*, **67**, 1845 (1963).

(5) H. R. Gerberich and W. D. Walters, *J. Am. Chem. Soc.*, **83**, 3935, 4884 (1961).

(6) Work of P. C. Rotoli in this laboratory.

(7) H. L. Herzog and E. E. Buchman, *J. Org. Chem.*, **16**, 99 (1951).

(8) F. Lautenschlaeger and G. F. Wright, *Can. J. Chem.*, **41**, 863 (1963).

(9) E. Wedekind and W. Weisswange, *Ber.*, **39**, 1631 (1906).