(33) J. J. Hinkel and J. P. Devlin, *J. Chem. Phys.*, **48**, 4750 (1973).
(34) K. Kaya, A. Nakatsuka, N. Kubota, and M. Ito, *J. Raman Spectrosc.*, **1**, 595 (1973).
(35) R. P. Van Duyne, D. L. Jeanmaire, and D. F. Shriver, *Anal. Chem.*, **46**, 213 (1974).
(36) R. P. Van Duyne, *J. Am. Chem. Soc.*, **95**, 7164 (1973).
(37) R. P. Van Duyne and D. L. Jeanmaire, 1974, unpublished results.
(38) R. P. Van Duyne and D. L. Jeanmaire, to be published.

Laser-Induced Fluorescence Studies of Alkali Metal Atom–Carbon Tetrahalide Matrix Reaction Products. Fluorescence Spectra of CBr_2 and CClBr in Solid Argon at 15°K

David E. Tevault and Lester Andrews[*1]

Contribution from the Chemistry Department, University of Virginia, Charlottesville, Virginia 22901. *Received August 26, 1974*

Abstract: CBr_2 and CClBr have been prepared by matrix reactions of alkali metal atoms with the appropriate tetrahalomethanes. Intense red fluorescence spectra from each of these carbenes have been recorded using 5682-Å excitation from a krypton ion laser. Analysis of the CBr_2 fluorescence spectrum observed following metal atom reactions with CBr_4 and $CClBr_3$ in argon gave a value of 196 cm^{-1} for the ground state bending mode. CClBr spectra were produced by metal atom reactions with CCl_2Br_2 in argon and a value of 257 cm^{-1} was determined for the ground state bending mode. Similar reactions of alkali metal atoms with CI_4 have failed to yield a fluorescence spectrum for CI_2.

Infrared spectra of dihalocarbene species have been extensively studied by the matrix-isolation technique. CBr_2, CClBr, and CCl_2 have been produced by alkali metal atom reactions with mixed bromine–chlorine tetrahalomethanes.[2] The latter two carbenes have also been isolated by pyrolysis of the appropriate $C_6H_5HgCX_3$ compound.[3] CF_2 and CCl_2 have been prepared by the reaction of photolytically produced carbon atoms with molecular fluorine and chlorine.[4,5] The infrared spectrum of CFCl was recorded following hard uv photolysis of CH_2FCl during deposition.[6] However, only CF_2 has been produced in sufficient quantity in a matrix environment to directly observe the bending mode, ν_2 at 668 cm^{-1}.[4]

Very recently, the bending modes of CFCl and CCl_2 have been determined from the laser-induced fluorescence spectra of the matrix-isolated species. The blue CFCl fluorescence, excited by near-uv laser lines, exhibited a 445-cm^{-1} spacing which was attributed to ν_2 of CFCl,[7] and the red CCl_2 fluorescence, stimulated by blue-green excitation, displayed as a 326-cm^{-1} interval.[8] Following this trend, CClBr, CBr_2, and CI_2 were expected to have fluorescence spectra excited by green, yellow, and red laser lines. The present report describes the observed CClBr and CBr_2 fluorescence spectra and the attempts to observe CI_2.

Experimental Section

Sample preparation, alkali metal atom, and spectroscopic techniques have been described in detail in previous publications from this laboratory.[7,9,10] CBr_4 (Eastman Organic Chemicals, Reagent) was purified by recrystallization from methanol, $CClBr_3$ was synthesized as described previously,[2a] CCl_2Br_2 (Eastern Chemical Co.) was shaken with elemental mercury to remove bromine impurities, and CCl_3Br (Aldrich, spectroscopic) and CI_4 (K & K Laboratories, Inc.) were used without purification. Lithium-7 (ORNL, 99.99%) and sodium (Baker, lump) were cut, rinsed with hexane, and loaded into the Knudsen cell immediately before the reaction vessel was evacuated. CI_4–argon samples were deposited by passing argon over CI_4 in a Pyrex tube heated to approximately 60°. CBr_4 and $CClBr_3$ matrix samples were prepared by allowing the vapor to equilibrate in a 2-l. can and adding argon gas. CCl_2Br_2 and CCl_3Br samples were prepared using standard manometric techniques.

Fluorescence spectra were recorded at 50 cm^{-1}/min and 1 cm/min chart speed on a Spex Ramalog. Spectra were excited using Coherent Radiation Model 52 G krypton and argon ion lasers and calibrated by superimposing laser emission lines.

Results

A weak red fluorescence spectrum was observed with 4880- and 5145-Å argon ion laser excitation of carbon tetrabromide–alkali metal matrix samples. Krypton ion laser excitation (5309 and 5682 Å) produced a better resolved and more intense fluorescence spectrum, which is shown in Figure 1 for the yellow excitation of a matrix prepared by the reaction of sodium atoms with an Ar–CBr_4 = 1000:1 sample. The most obvious feature of this spectrum is the progression of 17 sharp bands with approximately 196-cm^{-1} spacings, which are labeled *a* in Figure 1 and listed in Table I. Another less-extensive 196-cm^{-1} spaced progression with ten members was also observed with constant relative intensity to the main progression. This progression, which was most prominent at higher quantum numbers, is also listed in Table I and labeled *b* in Figure 1.

Figure 2 shows the fluorescence spectra resulting when alkali metal atom–argon mixed-tetrahalomethane samples were irradiated with 5682-Å krypton ion laser excitation. The top spectrum in this figure, produced following the reaction of $CClBr_3$ with sodium, is identical to that observed when alkali metal atoms were reacted with CBr_4. The bottom scan from the CCl_3Br reaction with sodium is the same spectrum but a factor of 20 weaker than the spectrum produced from alkali metal-CCl_4 and -CCl_3Br matrix samples irradiated with 5145-Å argon ion laser excitation;[8,11] 5682-Å excitation reaches the beginning of the CCl_2 absorption band[5] and, therefore, produces a weaker fluorescence spectrum than 5145 Å, which has a larger absorption coefficient. The bottom spectrum has been assigned to CCl_2 perturbed by another molecule in an adjacent matrix site.[8]

The middle spectrum, recorded with 5682-Å excitation following the matrix reaction of lithium atoms with CCl_2Br_2 in argon, consists of several progressions which are spaced by 257 cm^{-1}. This spacing is intermediate between

Table I. Dibromocarbene Fluorescence Progressions (cm^{-1}) in the Ground Electronic State Bending Mode, v_2''

a series $(0v_2'0) \rightarrow (0v_2''0)$	*b* series $(0(v_2' - 1)0) \rightarrow (0v_2''0)$
14,768	
14,574	
14,379	
14,182	
13,984	13,850[a]
13,790	13,656
13,596	
13,398	13,264
13,202	13,074
13,009	12,881
12,816	12,685
12,620	12,490
12,425	12,300
12,235	12,102
12,040	11,915
11,850	11,719
11,664	

[a] Values of *a* and *b* series members on the same horizontal line have the same value of v_2''.

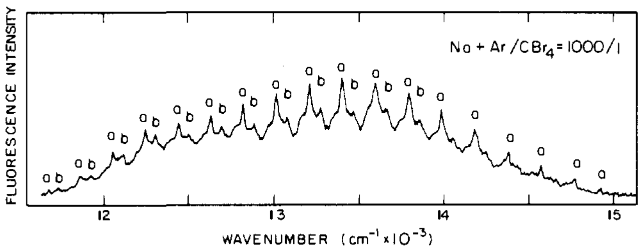

Figure 1. Dibromocarbene fluorescence spectrum produced by 5682 Å krypton ion laser excitation of a matrix sample prepared by the codeposition of sodium atoms and an Ar-CBr_4 1000:1 gas mixture on a copper wedge at 15°K.

that observed for CCl_2 (326 cm^{-1}) and CBr_2 (196 cm^{-1}), and the peak intensity of the fluorescence system, 13,800 cm^{-1}, comes intermediate between that assigned to CCl_2 (14,800 cm^{-1})[8] and that observed for CBr_2 (13,400 cm^{-1}). This trend is also depicted in Figure 2. Excitation (5145 Å) of the CCl_2Br_2 sample produced a weak spectrum similar to the one at the bottom of Figure 2. The bands observed in the lithium atom-CCl_2Br_2 spectrum excited by 5682-Å light are grouped into the several 257-cm^{-1} progressions and listed in Table II.

An attempt was made to produce similar spectra with 5682- and 6471-Å krypton ion laser excitation of alkali metal atom-CI_4 samples. No structured fluorescence spectra were produced with these exciting lines. Laser excitation (5309 Å) gave the resonance Raman progression of isolated I_2 originating at 212 cm^{-1} [12] which presumably arises from laser-induced photodecomposition of CI_4.

Discussion

The assignment of the fluorescence spectra depicted in Figure 2 to CBr_2, CClBr, and CCl_2, respectively, follows closely the results of similar studies on CFCl and CCl_2.[7,8] Carbenes have very strong, structured electronic absorptions which have been observed in inert gas matrices. The CF_2 absorption maximizes at around 2500 Å,[4] CFCl peaks at about 3500 Å,[6] and CCl_2 at about 5000 Å.[5] By extension, it was predicted that CClBr and CBr_2 probably have absorption maxima at lower energy (5500-6000 Å).

In recent studies, matrix fluorescence spectra of CFCl[7] and CCl_2[8] have been observed following matrix reactions of alkali metal atoms with $CFCl_3$ and CCl_4, respectively. When these samples were irradiated with 3500- and 5000-Å laser light, very extensive progressions in the ground state bending modes were recorded. The analogous reactions with CBr_4 (Figure 1) and $CClBr_3$ (Figure 2) have produced a 5682-Å excited fluorescence spectrum with 196-cm^{-1} spacings which is attributed to the bending mode of ground state CBr_2. The CCl_2Br_2 reaction product spectrum (Figure 2) contained five progressions with a 257-cm^{-1} spacing which is appropriate for the ν_2 mode of CClBr.

The carbenes were produced as the final product of reactions 1 and 2. The primary reaction product CBr_3 radical

$$CBr_4 + M \longrightarrow MBr + \cdot CBr_3 \qquad (1)$$

$$\cdot CBr_3 + M \longrightarrow MBr + :CBr_2 \qquad (2)$$

and the secondary product CBr_2 have been observed in infrared spectra of similarly prepared samples.[2a]

Supporting evidence for assignment of the observed spectra to the carbene products and not trihalomethyl radicals is provided by the fact that three, and only three, different fluorescence spectra were observed using 5682-Å excitation of samples prepared by alkali metal reactions with CBr_4, CCl_3Br, CCl_2Br_2, CCl_3Br, and CCl_4. These three different spectra are shown in Figure 2. Three unique dihalocarbene species, CBr_2, CClBr, and CCl_2, were produced by the cocondensation reaction. The fluorescence spectrum observed depends upon the yield of a particular CX_2 species. Although both CBr_2 and CClBr have been observed in the infrared spectrum of $CClBr_3$ reaction products,[2a] the yield of CBr_2 is apparently higher and the CBr_2 fluorescence dominates the top spectrum in Figure 2. Likewise, the CCl_2Br_2 reaction produces all three CX_2 species, but the CClBr yield is highest and the CClBr fluorescence is most intense with 5682-Å excitation which is strongly absorbed by CClBr. The middle spectrum in Figure 2 probably contains underlying signal due to CBr_2 and CCl_2; in fact 5145-Å ex-

Table II. Chlorobromocarbene Fluorescence Progressions (cm^{-1}) in the Ground State Bending Mode, v_2''

a series[a] $(0v_2'0) \rightarrow (0v_2''0)$	*b* series $(0(v_2' + 1)0) \rightarrow (0v_2''1)$	*c* series $(0v_2'0) \rightarrow (0v_2''1)$	*d* series $(0v_2'0) \rightarrow (0v_2''2)$	*e* series $(0v_2'0) \rightarrow (1v_2''(0)$
15,778[a]	15,362	15,174		
15,523	15,110	14,918	14,314	
15,273	14,852	14,660	14,064	
15,006	14,595	14,402	13,802	
14,750		14,141	13,544	14,012
14,495		13,904		13,762
14,244	13,841	13,654		13,514
13,984	13,574	13,402		13,260
13,726	13,322	13,157		13,006
13,465	13,063	12,885		
13,210	12,812			
	12,560			

[a] Individual progression members on the same horizontal line have the same value of ground state bending mode quantum number, v_2''.

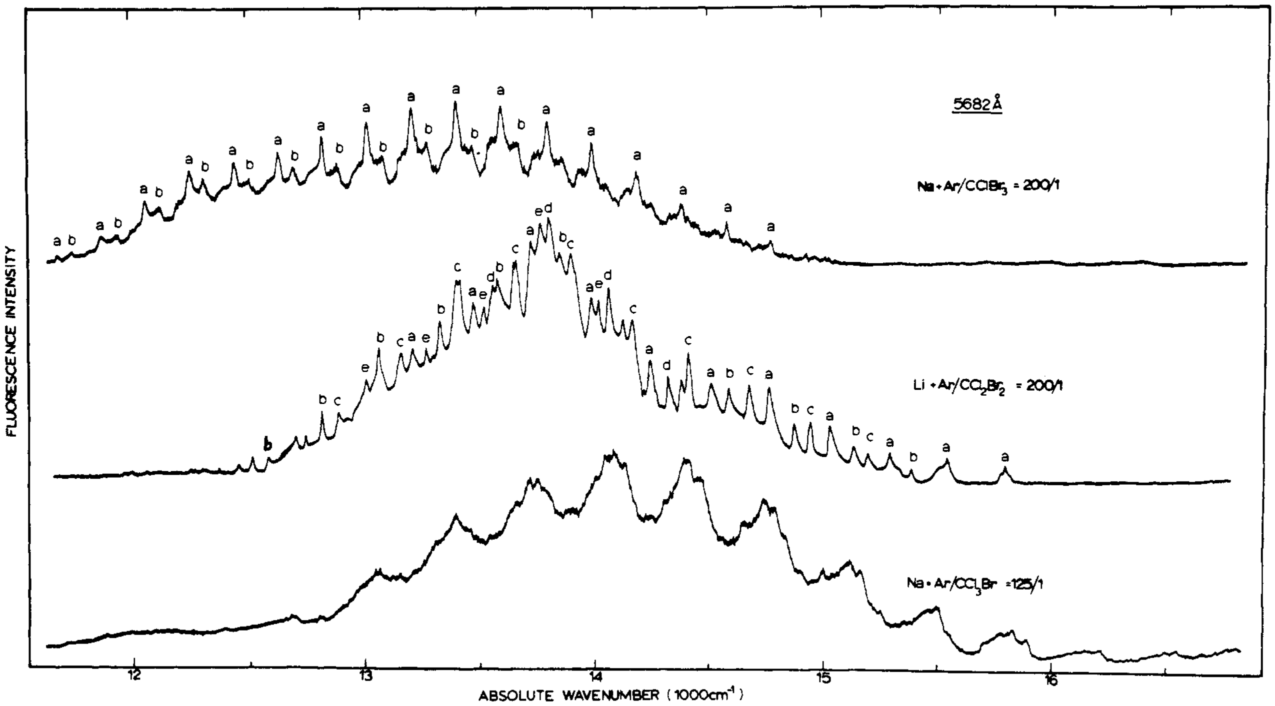

Figure 2. Laser-induced fluorescence spectra (5682 Å) of CBr_2, CClBr, and CCl_2 in solid argon produced by alkali metal atom matrix reactions with $CClBr_3$, CCl_2Br_2, and CCl_3Br, respectively, at high dilution in argon.

citation of this sample, where perturbed CCl_2 absorbs more strongly than CClBr, produced the perturbed CCl_2 fluorescence with lower intensity. The bottom spectrum is dominated by the fluorescence from perturbed CCl_2; CClBr, although surely present, did not make a resolvable contribution to the fluorescence spectrum.

On the other hand, if CX_3 were the carrier instead of CX_2, four separate fluorescence patterns would have been produced by CBr_3, $CClBr_2$, CCl_2Br, and CCl_3, which were observed in the corresponding infrared spectra from the five CX_4 precursors.[13] However, only three distinct fluorescence patterns were found in the present studies, and accordingly, the fluorescence must be caused by the dihalocarbene species.

The main CBr_2 fluorescence system *a* has 17 clearly distinguishable bands. These represent transitions from a common excited electronic state vibrational level into a ground state progression involving the bending mode of CBr_2. A similar study of the matrix CCl_2 fluorescence has revealed ground state progressions in both symmetric fundamentals, ν_1 and ν_2. Even if the ν_1 transitions are present (and they should be), ν_1 series could not be distinguished from the ν_2 progression since ν_1 of CBr_2 is 595 cm^{-1},[2a] almost exactly three times the ν_2 value of 196 cm^{-1}. The natural bandwidths (20 cm^{-1}) would not allow the resolution of bands terminating in final states represented by $(0v_20)$ and $(1(v_2 - 3)0)$. In other words, it is not possible to observe ν_1 in the presence of $3\nu_2$.

The other 196-cm^{-1}-spaced progression in the CBr_2 fluorescence spectrum has ten clearly resolved members and appears as a 60 cm^{-1} higher energy counterpart of the main ν_2 progression. A consistent assignment is that the weaker progression originates in a more vibrationally quenched level of the upper state. For example, if the main *a* progression is assigned to $(010) \rightarrow (0v_20)$ transitions, then the weaker *b* progression could be the $(000) \rightarrow (0(v_2 - 1)0)$ transition. The lack of spacing change between the *a* and *b* series is confirming evidence that the *b* series does not involve ground state bond stretching vibrations since a large anharmonicity correction and a spacing change would be expected for stretching modes.[7] This interpretation (196-60 cm^{-1}) gives a spacing of about 136 cm^{-1} for ν_2', the excited state bending mode of CBr_2, which is in accord with those of CCl_2 (305 cm^{-1}),[8] CFCl (405 cm^{-1}),[7] and CF_2 (496 cm^{-1})[14] in that the spacing of the upper state bending mode is less than that of the ground state.

For the purpose of vibrational analysis, it may be assumed that the first observed CBr_2 fluorescence band at 14,768 cm^{-1} terminates in the (010) final state. Extrapolation by 196 cm^{-1} places the (000) final state emission at 14,964 cm^{-1}. The "*a*" series bands were plotted as $(G(0v_20) - 14{,}964)/(v_2)$ vs. the v_2 quantum number.[15] This plot gives a harmonic value for the CBr_2 bending mode of 196.2 ± 0.2 cm^{-1} and an anharmonic X_{22} value of −0.08 ± 0.02 cm^{-1}. It should be emphasized that the final state designations for the fluorescence bands are not known; however, the first band observed at 14,768 cm^{-1} probably terminates in a state within a few quanta of the completely quenched (000) state.

The CClBr fluorescence spectrum is comparable to that observed[7] for CFCl. The unsymmetrical carbenes are different from CCl_2 and CBr_2 in that the vibronic selection rules allow all three of the ground state vibrational modes to mix in the electronic transitions. This fact is evidenced by the much more complicated CClBr spectrum as compared to CBr_2. In the case of CFCl, several emitting states were found to fluoresce into the ground state progressions $(0v_20)$, $(1v_20)$, and $(1v_21)$. CClBr seemingly involves primarily one emitting state, but several ground state progressions with a 257-cm^{-1} spacing can be identified. These are listed in Table II. The *a* series in Table II involves only transitions from the upper state to the $(0v_20)$ ground state levels, where ν_1 is the C–Cl stretch, ν_2 is the bend, and ν_3 is the C–Br stretch. Fortunately, the matrix-infrared spectrum[3] for CClBr has produced the ν_1 and ν_3 assignments of 744 and 612 cm^{-1}. The *a* series data indicate a very small anharmonic constant $X_{22} \sim 0$ cm^{-1}.

The $a(v_2) - c(v_2)$ differences range from 613 to 580 cm^{-1} as v_2 increases; this is in excellent agreement with the C–Br mode. The decrease in difference arises from the anharmonic cross-term X_{23} in the potential energy expression which has a value of approximately −2.5 cm^{-1} for CClBr.

Accordingly, the *c* series is assigned to a progression from the same upper state to the ground state levels $(0v_21)$.

Differences between the *a* and *e* series range from 738 to 720 cm^{-1} in very good agreement with the C–Cl mode of CClBr; the decrease comes from the anharmonic term X_{12} which is approximately -5 ± 2 cm^{-1}. The *e* series is assigned to the progression terminating in $(1v_20)$ levels. The *c* and *e* series energies, relative to the *a* series, confirm that the carrier of the fluorescence spectrum is CClBr.

The short *d* series of four members are spaced another quantum of the C–Br mode above the *c* series. The *d* series is attributed to the $(0v_20) \rightarrow (0v_22)$ fluorescence and it provides an X_{33} estimate of -1 cm^{-1}.

The *b* series is spaced approximately 190 cm^{-1} higher energy from the *c* series. This energy is appropriate for the excited state bending mode spacing. Therefore, the *b* series is assigned to the "excited state" progression $(0(v_2+1)0) \rightarrow (0v_21)$ counterpart to the *c* progression $(0v_20) \rightarrow (0v_21)$. The six lower energy *b* bands may in fact belong to a different progression than the four higher energy *b* bands; the present data are incapable of ruling out this possibility.

Two unlabeled bands at 14,372 and 14,113 cm^{-1} may also belong to CClBr since they exhibit the correct spacing, but without more members, this short "series" cannot be identified. Likewise weak bands on the low energy tail at 12,730, 12,680, 12,470, and 12,430 cm^{-1} may belong to other progressions of CClBr which cannot be defined without additional data.

The fact that the fluorescence spectra of the CX_2 species show long, strong progressions in the bending mode indicates a large change in valence angle between the ground and excited electronic states. The valence angles for the ground (105°) and excited (122°) electronic states of CF_2[14] are indicative of the geometries of these states for the heavier CX_2 species.

It is interesting to speculate on the failure to observe a fluorescence for CI_2. CI_2 is probably produced by the iodocarbon analogs[16] of reactions 1 and 2. However, CI_2 could be photodecomposed by the laser excitation. If the analogous electronic band for CI_2 were between 5682 and 6471 Å or to the red of 6500 Å, the presently available krypton plasma laser lines could not excite the fluorescence.

Conclusions

CBr_2 and CClBr have been synthesized by matrix reaction of CBr_4, $CClBr_3$, and CCl_2Br_2 with alkali metal atoms. Fluorescence spectra excited with 5682 Å krypton ion laser light have revealed two progressions in the ground state bending mode for CBr_2 (196 cm^{-1}) which emanate from two different bending mode levels of excited CBr_2; these emitting levels cannot be definitely assigned. The CClBr spectrum was only observed using the CCl_2Br_2 precursor suggesting nearly equal reactivities of chlorine and bromine with alkali metal atoms. Owing to the lower symmetry of CClBr, its fluorescence spectra were more complex than the CBr_2 spectra. Progressions in the CClBr ground state bending mode (257 cm^{-1}) were observed with and without combinations of the C–Br and C–Cl stretching modes.

Acknowledgment. The authors gratefully acknowledge financial support for this research by the National Science Foundation under Grant GP-38420X and an Alfred P. Sloan Fellowship for L.A.

References and Notes

(1) Author to whom correspondence should be addressed.
(2) (a) L. Andrews and T. G. Carver, *J. Chem. Phys.*, **49**, 896 (1968); (b) L. Andrews, *ibid.*, **48**, 979 (1968).
(3) A. K. Maltsev, O. M. Nefedov, R. H. Hauge, J. L. Margrave, and D. Seyferth, *J. Phys. Chem.*, **75**, 3984 (1971).
(4) D. E. Milligan and M. E. Jacox, *J. Chem. Phys.*, **48**, 2265 (1968).
(5) D. E. Milligan and M. E. Jacox, *J. Chem. Phys.*, **47**, 703 (1967).
(6) C. E. Smith, D. E. Milligan, and M. E. Jacox, *J. Chem. Phys.*, **54**, 2780 (1971).
(7) D. E. Tevault and L. Andrews, *J. Mol. Spectrosc.*, **54**, 54 (1975).
(8) D. E. Tevault and L. Andrews, *J. Mol. Spectrosc.*, **54**, 110 (1975).
(9) D. A. Hatzenbuhler and L. Andrews, *J. Chem. Phys.*, **56**, 3398 (1972).
(10) L. Andrews, *J. Chem. Phys.*, **57**, 51 (1972).
(11) J. S. Shirk, *J. Chem. Phys.*, **55**, 3608 (1971).
(12) W. F. Howard, Jr., and L. Andrews, *J. Raman Spectrosc.*, in press.
(13) L. Andrews, *J. Chem. Phys.*, **48**, 972 (1968).
(14) C. W. Mathews, *Can. J. Phys.*, **45**, 2355 (1967).
(15) For a quantitative treatment of vibrational energies, see G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," Van Nostrand, New York, N.Y., 1945, p 205.
(16) D. W. Smith and L. Andrews, *J. Phys. Chem.*, **76**, 2718 (1972).

Steric Hindrance in Potassium Atom-Oriented Molecule Reactions. Methyl Iodide and *tert*-Butyl Iodide

George Marcelin and Philip R. Brooks*[1]

Department of Chemistry, Rice University, Houston, Texas 77001. *Received August 29, 1974*

Abstract: The reaction of K atoms with oriented CH_3I or t-C_4H_9I molecules has been studied via the crossed molecular beam method. Oriented molecules are produced by passing a molecular beam through an inhomogeneous electric field which rejects unwanted orientations. The remaining molecules are oriented with respect to a weak electric field and can be reversed in the laboratory by changing the direction of the applied field. The reaction is studied for impact at the two ends of the molecule and for both reactions the iodine end is most reactive. A simple model is used to interpret the results and suggests that the hindering size which can be ascribed to the R groups is only roughly compatible with van der Waals radii.

Very few gas phase bimolecular chemical reactions proceed on every gas kinetic-collision. Most reactions have an activation energy which (presumably) restricts reaction to those collisions with energy greater than the activation energy, E_a. But counting only those collisions with energy greater than E_a still gives a rate faster than the rate of almost any chemical reaction. To account for this discrepancy between theory and fact the notion was advanced that only certain orientations of the reagents were effective in promoting reaction, and the "steric factor", ρ, was introduced as the fraction of gas-kinetic collisions which had the right orientation to react.