

planation for both of these observations. The lowest energy structure (Figure 11), as well as six others of very similar conformation and only slightly higher calculated energy, all show the tryptophan NH to be internally buried and the methyl group of the alanine residue marked Ala<sub>8</sub> in Figure 11 to be in the shielding region of the tryptophan ring. It appears that phalloidin is a relatively rigid molecule in solution.

### Conclusion

A number of other cyclic polypeptides are currently under study in our laboratory in collaboration with

other groups. Complete conformational structures are not yet available for these molecules, which include the neurohypophyseal hormones oxytocin<sup>66,67</sup> and lysine-vasopressin<sup>68,69</sup> and related precursors and partial structures.

(66) V. J. Hruby, A. I. Brewster, and J. A. Glasel, *Proc. Nat. Acad. Sci. U. S.*, **68**, 450 (1971).

(67) A. I. Brewster, J. A. Glasel, and V. J. Hruby, *ibid.*, in press.

(68) P. H. Von Dreele, A. I. Brewster, H. A. Scheraga, M. F. Ferger, and V. du Vigneaud, *ibid.*, **68**, 1028 (1971).

(69) P. H. Van Dreele, A. I. Brewster, F. A. Bovey, H. A. Scheraga, M. F. Ferger, and V. du Vigneaud, *ibid.*, **68**, 3088 (1971).

## Chemical Applications of Optical Pumping

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The chemist is a guest at the physicist's table, and he frequently dines well, *viz.*, X-rays, nuclear magnetism, induced emission, recoilless  $\gamma$ -rays, . . . . The optical pumping phenomenon, that is, the orientation of atomic electronic spins through the use of circularly polarized light, may, by analogy, also be interesting to chemists: optical pumping is a method for studying a special class of free radicals. Free radicals have been studied by an array of techniques, *e.g.*, their catalysis of the conversion of ortho- to para-hydrogen (1920's), removal of a metallic mirror (1930's), and electron spin resonance. The latter method is so powerful that one may wonder what else could possibly be added. The answer is that esr is of limited sensitivity. For example, chemically induced nuclear spin polarization is one way of measuring the effects of radicals which live for only  $10^{-9}$  sec. By optical pumping the hyperfine structure of special radicals can be measured with greater precision and the radical can be detected at much lower concentrations than with esr.

Optical pumps (scientists who optically pump) measure two types of properties—those of the excited states of atoms and molecules inferred from their fluorescence, and the properties of the ground state. We want to concentrate here on the generation, stability, and usefulness of a ground-state ensemble of spin-oriented atoms. A gas-phase atom is characterized by a total angular momentum  $\vec{J}$ , the sum of the electronic orbital and spin angular momenta and a quantized component,  $J_z$ . The spin angular momentum is in general reoriented only by magnetic fields, but the orbital an-

gular momentum is easily reoriented by the electric fields which act during a collision. To prevent destruction of the spin orientation within a few collisions the ground state of the atom must have  $J = 1/2$  (groups Ia, Ib, and IIIa of the periodic table) or if  $J > 1/2$ ,  $L$  must be 0 (groups V, VIIb, and VIb except for W). For experimental convenience most work has been done with the alkali atoms which have  $^2S_{1/2}$  ground states.

### Generation of a Gas of Spin-Oriented Atoms

A particular example will suffice to show what optical pumping is. Consider a hypothetical atom with zero nuclear spin and a single valence electron. Its energy levels in a small magnetic field are shown in Figure 1. Let us apply a beam of right circularly polarized light in the same direction ( $z$ ) as a magnetic field; the wavelength of the light is chosen so that it excites only the  $^2P_{1/2}$  state. The light wave carries angular momentum in the  $z$  direction, and when it is absorbed the angular momentum of the atom must increase, *i.e.*,  $\Delta M = +1$  where  $M$  is the magnetic quantum number. Only the  $-1/2 \rightarrow 1/2$  transition is allowed. The excited  $M = 1/2$  state can undergo radiative or nonradiative (collisional quenching) transitions to the ground state. If the atom returns to the ground state  $M = -1/2$  state nothing is gained or lost. If it goes to the ground state  $M = 1/2$  state, it will remain there for some time until spin relaxation takes place. This results in a large excess of atoms in the  $M = 1/2$  state. In favorable cases the net spin orientation of the gas can exceed 90%. As an atom in the  $M = 1/2$  state cannot absorb the right circularly polarized light, the spin orientation can be inferred from optical absorption experiments. One does not need to perform electron spin resonance to determine the spin orientation.

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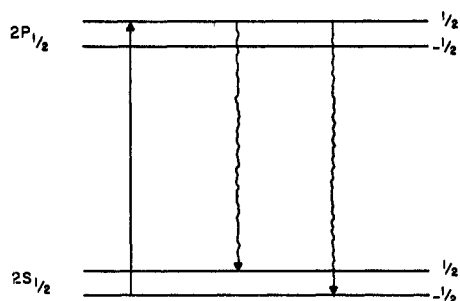


Figure 1. Absorption with  $\Delta M = +1$  and spontaneous emission.

Atoms are usually pumped with their own resonance radiation; to keep the optical density of the cell less than one, the atomic pressure is maintained at  $10^{-5}$  mm or less. At these pressures the atoms bounce back and forth between the walls. The material of most walls absorbs a thin layer of the atoms which efficiently disorient the gas-phase atoms when they collide. (Long-chain hydrocarbons, particularly deuterated hydrocarbons,<sup>1</sup> are an exception.) In general, then, to achieve an appreciable optical pumping, it is necessary to add about 0.1 atm of a so-called buffer gas which retards diffusion to the wall. The buffer gases must be exceedingly inert, the favorite ones being  $N_2$ , He, Ne, and Ar.

### Stability of Orientation

The absorption of circularly polarized resonance light, as mentioned above, is a measure of the orientation of the ensemble. Therefore, a simple way<sup>2</sup> to study the stability of orientation of the ensemble is to shut off the pumping light and then turn it on again, measuring the change in transmission of the cell as a function of the time in which the pumping light is off. For a typical cell of dimensions of the order of centimeters and for a typical buffer gas pressure of the order of 10–40 Torr, the relaxation time of the total  $z$  component of the electron spin  $\langle S_z \rangle$  is of the order of tenths of a second. In magnetic resonance the relaxation rate of  $\langle S_z \rangle$  is usually quoted because it has molecular significance. In optical pumping, unless the cell walls have been specially treated, wall relaxation is an important part of the relaxation so it is only useful to quote the part of the rate which is independent of the walls.

Until recently the data on electron spin relaxation in optical pumping have been analyzed by assuming that the wall-independent relaxation rate was given by

$$-\frac{d\langle S_z \rangle}{dt} = k_0 p_B \langle S_z \rangle$$

where  $k_0$  is a rate constant and  $p_B$  is the pressure of buffer gas molecules. From kinetic theory

$$k_0 = \langle v_{rel} \rangle \sigma (kT)^{-1}$$

where  $v_{rel}$  is  $(8kT/\pi\mu_{AB})^{1/2}$  and  $\mu_{AB}$  is the reduced mass of the alkali atom–buffer gas molecule pair. Thus a

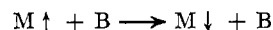
(1) M. A. Bouchiat and J. Brossel, *Phys. Rev.*, **147**, 41 (1966).  
 (2) W. Franzen, *ibid.*, **115**, 850 (1959).

Table I  
Cross Sections ( $\text{cm}^2$ ) for Flipping of Alkali Spins  
by Various Molecules<sup>a</sup>

	Na	K	Rb	Cs
He	$2.2 \times 10^{-26}$	$1.1 \times 10^{-25}$	$3.3 \times 10^{-25}$	
H <sub>2</sub>	$2.7 \times 10^{-26}$		$3 \times 10^{-24}$	
CH <sub>4</sub>			$8 \times 10^{-24}$	
C <sub>2</sub> H <sub>6</sub>			$3.8 \times 10^{-23}$	
Ne	$1.8 \times 10^{-24}$		$3.3 \times 10^{-24}$	$5.3 \times 10^{-24}$
N <sub>2</sub>	$4.1 \times 10^{-24}$		$5.7 \times 10^{-23}$	$7.0 \times 10^{-23}$
Ar	$8.8 \times 10^{-23}$		$1.1 \times 10^{-22}$	$8.0 \times 10^{-23}$
C <sub>6</sub> H <sub>12</sub>			$4.5 \times 10^{-22}$	
Kr	$2.0 \times 10^{-21}$		$7.3 \times 10^{-21}$	$2.1 \times 10^{-21}$
Xe	$2.5 \times 10^{-20}$		$1.3 \times 10^{-19}$	$4.6 \times 10^{-20}$
C <sub>6</sub> H <sub>6</sub>			$6 \times 10^{-19}$	$4.7 \times 10^{-18}$
O(CH <sub>3</sub> ) <sub>2</sub>			$3 \times 10^{-18}$	
O(CH <sub>2</sub> ) <sub>4</sub> O			$4 \times 10^{-18}$	
NH <sub>3</sub>			$8 \times 10^{-18}$	

<sup>a</sup> The space separates atoms and molecules with  $\sigma$  below and above  $10^{-21} \text{ cm}^2$ . In the latter case optical pumping is impossible when the buffer gas is present at a pressure  $\geq 1$  Torr. Data are from ref 3, 4, and 5.

spin-flip “cross section,”  $\sigma$ , was extracted and a representative set is shown in Table I. This cross section is for the process



The spin angular momentum change must be compensated by an opposite change of angular momentum of the nuclear framework of M and B. This is an unlikely process, and it is therefore not surprising that the cross sections are small.

The data<sup>2–5</sup> contained in Table I and other experiments lead to the following conclusions. Optical pumping of alkali atoms is impossible when there is present more than a trace amount of gases whose molecules have high atomic number (Kr, Xe), strongly polar groups (NH<sub>3</sub>, (CH<sub>3</sub>)<sub>2</sub>O, dioxane), or  $\pi$  electrons (benzene, naphthalene). The heavy-atom relaxation is caused by the interaction of the electron spin with the angular momentum of the “quasi-molecule” formed during the collision. A theory for this spin–orbit effect has been worked out by Herman,<sup>6</sup> who pointed out that deformation of the alkali atom wave function during collision is required for the interaction to be important. He obtained order of magnitude agreement with the observed cross sections by an approximate calculation.

The even larger spin-flip cross sections of the polar and aromatic molecules which contain no heavy atoms raise a difficult physical problem with a chemical solution. The spin-flip processes must ultimately be due to the interaction of the magnetic moment of the spins with a magnetic field. The magnetic field coming from the nucleus is too small to account for the large spin-flip “cross sections.” The external magnetic

(3) R. J. McNeal, R. A. Bernheim, R. Bersohn, and M. Dorfman, *J. Chem. Phys.*, **40**, 1678 (1964).

(4) R. J. McNeal, *ibid.*, **40**, 1089 (1964); **37**, 2726 (1962).

(5) R. A. Bernheim, “Optical Pumping, An Introduction,” W. A. Benjamin, New York, N. Y., 1965.

(6) R. M. Herman, *Phys. Rev. A*, **136**, 1576 (1964).

field in the experiment is usually so small (a few gauss) that the interaction of the spin with the external magnetic field, made anisotropic during a collision, is again far too small. In a system with only one unpaired electron, the only remaining source of magnetic field is the orbital motion of the electrons. In the molecules with only light atoms this is again too small.

The solution to this dilemma is fascinating. The larger cross sections in Table I are probably not cross sections at all. The major part of the relaxation effect of the gases in the lower half of Table I is *not* caused by a collision of an alkali atom with a buffer gas molecule; it is caused instead by the collisions of the complex of the alkali atom and the molecule with another molecule. The complex is formed by polarization forces, dipole-induced-dipole forces, or in the case of benzene perhaps even charge transfer. The complex formation is such an effective mechanism for relaxation because the spin-orbit interaction acts not just in the  $10^{-13}$  sec duration of a collision but in the interval between the formation of the complex and its destruction, presumably on the next collision  $\sim 10^{-8}$  sec later.

The proof that these complexes exist is not merely that there is no other reasonable explanation. Recently, Bouchiat, Brossel, and Pottier<sup>7</sup> have shown that for Rb atoms in a Kr buffer gas, the relaxation equations may be written<sup>8</sup>

$$\frac{-d\langle I_z \rangle}{dt} = k_1 p_B \langle I_z \rangle + \frac{k_2 p_B^2}{a + p_B^2} \langle I \rangle$$

where  $a$  is proportional to the square of the magnetic field and  $k_1$ ,  $k_2$  are constants. This theoretical expression was suggested and confirmed by experimental results. The first relaxation term, linear with pressure, is due to the spin-orbit interaction which operates during the collision of buffer gas and alkali atoms, *i.e.*, in the quasi-molecule. The second term, depending peculiarly on the pressure, is due to a *real* molecule, *i.e.*, the complex. The spin-orbit interaction of the Rb-Kr molecule is interrupted by a collision, presumably destructive, with a Kr atom. Under the conditions of their experiment only about one Rb atom in  $10^6$  was complexed and yet at low magnetic fields the second term dominated the relaxation. This is, by far, the most specific experiment yet performed on a van der Waals complex. The strong magnetic field dependence of the relaxation rate was the key to the proof; similar investigations should be carried out on other molecules that form complexes.

### Utility of the Ensemble

**Pressure Shift of the Magnetic Hyperfine Interaction.** When molecules collide, in principle, a transient deformation of the charge distribution should occur

(7) M. A. Bouchiat, J. Brossel, and L. Pottier, *Phys. Rev. Lett.*, **19**, 817 (1967).

(8) The nuclear spin component of the ensemble,  $\langle I_z \rangle$ , is used here rather than the electron spin component,  $\langle S_z \rangle$ . The reason is that at low magnetic field the angular momentum which is oriented is  $\vec{F} = \vec{S} + \vec{I}$  because the interaction of  $\vec{I}$  with  $\vec{S}$ , the hyperfine interaction,

**Table II**  
Fractional Hyperfine Frequency Shifts of Atoms  
in Various Buffer Gases<sup>a</sup>

	He	H <sub>2</sub>	Ne	Ar	Kr	Xe	C <sub>6</sub> H <sub>6</sub>
H (0°)	0.14	0.01	0.08	-0.13			
Li (390°)	5.29		2.76	-0.36			
Na (22°)	2.21	1.88	1.36	0.09	-1.27	-2.57	
K (65°)	3.23	2.50	1.80	-0.03	-3.16		
Rb (25°)	3.22	2.96	1.75	-0.23	-2.60		-66.6
Cs (30°)	5.41	6.43	2.20	-0.85	-4.39	-8.12	

<sup>a</sup> The numbers are  $[(1/A)\partial A/\partial n]_V$  in units of  $\text{\AA}^3$  where  $n$  is the number density of buffer gas molecules. Data for Li are from ref 10. Reference 5 gives the sources of the other data.

during the collision. This effect is most clearly seen in a modification of the magnetic hyperfine interaction constant,  $A$ , *i.e.*, in the spin density at the nucleus. If  $A(R)$  is the hyperfine constant of an atom at a distance  $R$  from the center of a buffer gas molecule, then in a dilute gas<sup>9</sup>

$$\langle A \rangle = A(\infty) + n \int [A(R) - A(\infty)] e^{-V(R)/kT} d\tau$$

where  $V(R)$  is the potential energy of the atom interacting with the buffer gas molecule whose number density is  $n$ . Table II<sup>10</sup> gives the values of the pressure shift expressed as an effective volume  $[1/A(\infty)]\partial\langle A \rangle/\partial n$ . A very simple picture emerges. At relatively large distances molecules polarize the alkali atom, thus promoting the s electron to non-s states which have zero density at the nucleus. This diminishes the hyperfine constant. On the other hand, at short distances the electronic shells begin to overlap and there is strong repulsion, hence an increase in hyperfine constant. From the data in Table II it is apparent for H<sub>2</sub> and the really light atoms, He and Ne, that the repulsion effects outweigh those of the polarization; for all other atoms and molecules polarization is more important.

Brewer<sup>11</sup> has made a very interesting measurement of the pressure shift, by far the largest known, of Rb in benzene. As he has pointed out, complexes formed by three-body collisions and subsequently destroyed by binary collisions are probably not the explanation. During each collision there is evidently a substantial reduction of the spin density at the Rb nucleus expressed by the function  $[A(R) - A(\infty)]$ . This sort of reduction is possible by van der Waals polarization as shown by the shifts of Kr and Xe. Indeed the polarizabilities of Kr, Xe, and benzene are  $2.48 \times 10^{-24}$ ,  $4.0 \times 10^{-24}$ , and  $10.3 \times 10^{-24}$  cm<sup>3</sup>, respectively; part of the difference between the pressure shifts of the three gases is accounted for. The most colorful explanation of the large pressure shift is that during the collision an electron jumps from the Rb atom to the benzene ring,

is stronger than the interaction of either  $\vec{I}$  or  $\vec{S}$  with respect to an external field. If  $\vec{F}$  is oriented, then both  $\vec{I}$  and  $\vec{S}$  are at least partially oriented, and it is somewhat more convenient to use  $\langle I_z \rangle$  in this experiment.

(9) G. A. Clarke, *J. Chem. Phys.*, **36**, 2211 (1962).

(10) J. R. Airey, E. F. Greene, G. P. Reck, and J. Ross, *ibid.*, **46**, 3295 (1967).

(11) R. G. Brewer, *ibid.*, **40**, 1077 (1964).

**Table III**  
Spin-Exchange Cross Sections<sup>a</sup>

Cs-Cs	$2.06 \times 10^{-14} \text{ cm}^2$
Rb-Rb	$1.84 \times 10^{-14} \text{ cm}^2$
K-K	$1.45 \times 10^{-14} \text{ cm}^2$

<sup>a</sup> Data are from N. W. Ressler, R. H. Sands, and T. E. Stark, *Phys. Rev.*, **184**, 102 (1969).

circumnavigates the benzene ring a few hundred times, and then jumps off again. Studies of the pressure shift with cyclohexane which has a polarizability of  $10.9 \times 10^{-24} \text{ cm}^3$  would test whether there was an effect more important than geometrical cross section and polarizability. Airey, Greene, Reck, and Ross have shown that the differential cross section for scattering of K atoms by benzene and cyclohexane is different. Benzene shows somewhat more scattering at larger angles which suggests a somewhat different effective potential energy surface. This is also indicated by the data in Table I which show that benzene is far more effective than cyclohexane in relaxing Rb spins.

**Spin Exchange.** In a weak magnetic field if two alkali metal vapors are mixed, say rubidium and cesium, their spin orientations will approach a common value. For example, if rubidium is pumped, inspection with cesium resonance radiation will show that cesium has also been pumped. Conversely, application of radiofrequency radiation at the cesium resonance frequency will destroy not only the cesium spin orientation but also that of the rubidium. The cross section for the process



has been found to be very large,  $\sim 200 \text{ \AA}^2$ . This magnitude shows that the term "spin exchange" is a misnomer; what we are seeing is electron exchange between electrons of opposite spin. The purely magnetic effect of spin flip without electron exchange is feeble compared to electron exchange. Typical spin-exchange cross sections are given in Table III.

The phenomenon of spin exchange offers the possibility of measuring the hyperfine structure of and detecting the pressure of transient, highly reactive species. For example,  $\text{H}_2$ ,  $\text{N}_2$ , and  $\text{P}_4$  have been dissociated in a discharge and the mixture of atoms and molecules led into an optical pumping cell where an alkali atom was being pumped. The characteristic hyperfine frequencies and pressure shifts of H, N, and P atoms have been measured in this way. Lambert<sup>12</sup> has shown that optical pumping at high temperatures is feasible, which greatly widens the range of atoms that can be studied.

### Free-Radical Detection in Photochemistry

**Total Free-Radical Concentration.** Spin exchange leads naturally to radical detection. Free radicals are produced with their spins disoriented. Thus on collision with the alkali atoms there will be an observable

(12) R. H. Lambert, *Phys. Rev.*, **183**, 180 (1969); *Phys. Rev. Lett.*, **22**, 161 (1969).

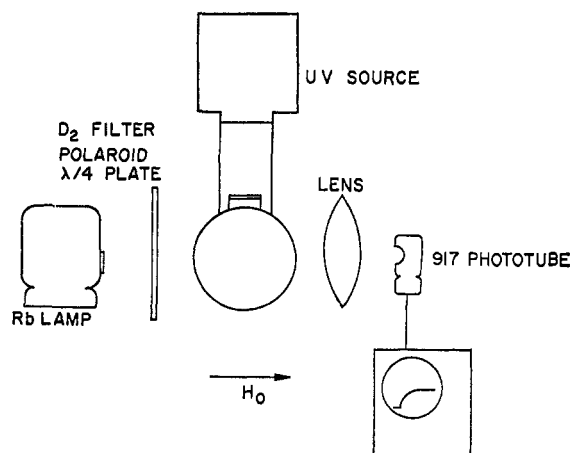
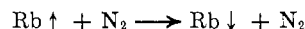


Figure 2. Optical pumping arrangement with provision for simultaneously photolyzing with vacuum uv. The  $\text{D}_2$  filter removes the Rb  $\text{D}_2$  line, increasing the amount of orientation attainable. The Polaroid sheet and quarter-wave plate produce circularly polarized light. Not shown are Helmholtz coils producing  $H_0$ , a radiofrequency coil around the cell, or connections to the gas system.

effect because of spin exchange. Referring to Table I we see that the cross section for the process



is  $10^{-22} \text{ cm}^2$  whereas for the process



the cross section (as mentioned above) is  $\sim 2 \times 10^{-14} \text{ cm}^2$  (Table III).

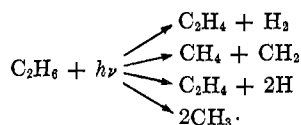
The rate of buffer gas disorientation is  $n_B v_B \sigma_{\text{spin flip}}$  and the rate of free-radical disorientation is  $n_R v_R \sigma_{\text{spin exch.}}$ . In these expressions  $v_B$  and  $v_R$  are average speeds of buffer gas molecules and free radicals relative to the alkali atoms. The important point is that, if the cross sections are in the ratio of  $\sim 10^8$ , the pressure of the radical which would have the same relaxation effect as the buffer gas would be a factor of  $10^8$  smaller, *i.e.*, about  $10^{-7} \text{ mm}$ . This is an upper limit to the radical pressure that could be measured; indeed if a coated cell were used with no buffer gas present, at least one order of magnitude improvement in sensitivity might be realized.

An interesting way to generate radicals is by light. In an experiment by Crosley<sup>13</sup> the target gas was mixed with the buffer gas and the alkali vapor and then three different sources of photons were turned on. Figure 2 shows a diagram of the apparatus. Vacuum uv photons enter the Pyrex flask through a LiF window to dissociate the target gas. Rubidium resonance radiation at  $7947 \text{ \AA}$  enters through a circular polarizer to pump the Rb vapor. Finally radiofrequency radiation in resonance with the Rb atom at the given magnetic field is passed through a coil surrounding the cell. The outstanding limitation of the method is that the molecule which is the parent of the radicals and the alkali atoms must be compatible, at least for a short time. This requirement eliminates almost all molecules unfortunately. The hydrocarbons, some fluorocarbons,

(13) D. R. Crosley, *J. Chem. Phys.*, **47**, 1361 (1967).

amines, and ethers appear to be the only classes of volatile compounds nonreactive with the alkalis.

Crosley carried out some preliminary experiments on radical detection in some simple hydrocarbons. The photochemistry of the simple hydrocarbons, methane, ethane, propane, etc., has been studied in detail by a number of workers. In each case there is a mixture of final products whose yield varies with wavelength. To explain the products a variety of initial modes of dissociation are postulated. Some of these modes involve the formation of radical fragments, others of molecular fragments, still others of biradicals. If one could measure the concentration of the intermediate radicals, some of the indefiniteness of the photochemistry would be removed. To be specific, consider the photolysis of  $C_2H_6$  which produces  $H_2$ ,  $CH_3$ ,  $C_2H_4$ ,  $C_2H_5$ , and  $C_4H_{10}$ . No less than four modes of dissociation have been proposed to explain the end products, *viz.*



Our knowledge of the role of the intermediates,  $CH_2$ ,  $H$ , and  $CH_3$ , is unsatisfactory. Methylene is believed to react on virtually any collision with the parent ethane, but  $CH_3$  and  $H$  persist for fractions of a second. It is these intermediates whose concentrations must be measured. To determine the total concentration of radicals one can measure the spin-lattice relaxation time of the oriented rubidium atoms. The first experiments on the simple hydrocarbons using Ar resonance radiation at 1067 Å yielded results for radical concentrations on the order of  $10^{10}/cm^3$ . Engineering problems prevented these measurements from being of quantitative significance, however. The principal problem is that the geometry of the vacuum uv beam is completely different from the interrogating Rb resonance radiation. Other problems involve establishing the precise pressure of the hydrocarbon, the

absolute uv intensity as a function of wave length, and the spin-exchange cross section.

One can be much more confident about the measurement of relative radical yields in different reactions than in the establishment of a precise quantum yield for radicals in a given photolysis.

**Detection of Individual Radicals.** *Hydrogen Atoms.* Crosley<sup>14</sup> observed the resonance of hydrogen atoms during the photolysis of ethane. While the absolute concentration of hydrogen atoms could not be measured precisely, it was estimated as  $\sim 10^9/cm^3$ . The spin-exchange determination of hydrogen atom concentrations is far superior to electron spin resonance and comparable to Lyman  $\alpha$  spectroscopy.<sup>15</sup> Actually, at low field, the resonance of deuterium atoms is at a different frequency from that of hydrogen atoms. The real power of the method will involve the measurements of the ratios of hydrogen to deuterium resonances during photolysis of such compounds as  $CH_2D_2$ ,  $CH_3CD_3$ ,  $CH_3CD_2CH_3$ , and  $(CH_3)_3CD$ .

*Free Radicals.* Polyatomic free radicals will certainly exchange electrons easily with alkali atoms. An  $\vec{S} \cdot \vec{J}$  interaction, not present in an atom but large in a molecule, will, unfortunately, destroy any orientation of the spin so the free radicals will not become spin oriented.

## Conclusions

Optical pumping of alkali atoms has given the chemist (1) a quantitative measure of the deformation of alkali atoms during collisions, (2) a method for detecting very weakly bound complexes of alkali atoms and molecules, (3) a method for detecting hydrogen atoms and for demonstrating the presence of free radicals during photolyses.

*The experimental work reviewed here was supported by the U. S. Atomic Energy Commission and by the U. S. Air Force. We are grateful to R. N. Zare for a critical reading of the manuscript.*

(14) D. R. Crosley and R. Bersohn, *J. Chem. Phys.*, **45**, 4353 (1966).

(15) W. P. Bishop and L. M. Doriman, *ibid.*, **52**, 3210 (1970).

# Reactivity of Heterocyclic Phosphorus Compounds

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## Studies of the reactivity of heterocyclic compounds

*Robert F. Hudson was born in Lincolnshire and educated at Imperial College, London. Appointed lecturer at Queen Mary College in 1947, he initiated work on acylation and phosphorylation, which he continued at Cyanamid European Research Institute, Geneva (1960). Professor Hudson was appointed to the chair of organic chemistry at the University of Kent at Canterbury in 1966, and was visiting professor at University of Rochester, 1970-1971. His present research interests include chemical reactivity, heterocyclic phosphorus and sulfur compounds, and radical rearrangements.*

*Charles Brown took up a Science Research Council Fellowship with Professor Hudson in 1967, where he worked on organophosphorus chemistry. He is presently a lecturer at Kent.*

and the influence of ring conformation have been invaluable in the evolution of mechanistic chemistry. In recent years the reactivity and stereochemistry of cyclic phosphorus compounds have received much attention, and investigations in this field have assisted greatly in our understanding of the behavior of fluxional molecules.

Our approach,<sup>1</sup> based on the original work of West-

(1) R. F. Hudson and R. Greenhalgh, *Chem. Commun.*, 1300 (1968).