Direct and Sensitized Photolyses of Various Dichlorobutanes[1]

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Abstract: The direct photolysis of neat 1,4-, 1,3-, 1,2-, and 2,3-dichlorobutanes (DCB) at 2537 Å, yielding HCl as a principal product, was investigated and compared with the corresponding radiolyses reported in the literature. Significant photoinduced 1,4 → 1,3 isomerization was observed in neat 1,4-DCB, but only minor rearrangements were detected in the photolysis of the other DCB's. The quantum yield ratio, $\Phi(\text{isom})/\Phi(\text{HCl})$, in the photolysis of neat 1,4-DCB ($\sim$2.6) was similar to that ($\sim$2.8) observed in the radiolysis of this same compound. The $\Phi(\text{HCl})$ and $G(\text{HCl})$ values for neat 1,3-DCB were found to correlate well with corresponding literature data for polyvinyl chloride. Sensitization of the photolysis of 1,4- and 1,3-DCB by acetone at 3130 Å gave the same major products as the direct photolysis. The mechanism of the sensitized photolysis is considered to involve collisional deactivation by DCB molecules of excited singlet states of acetone.

Although the photodehydrochlorination of vinyl chloride polymers has been studied extensively,[3] certain aspects of the mechanism remain unsettled. For example, the nature and source of the initiation step in the photolysis of polyvinyl chloride (PVC) require clarification. Also, the possibility that trace impurities of the carbonyl type (present in the polymer backbone or in the form of residual solvent) can photosensitize the dehydrochlorination reaction needs to be assessed.[4] The present paper is concerned with an attack on these questions through a study of both the direct and sensitized photolyses of various dichlorobutanes as (liquid) model compounds of the vinyl chloride polymers. Apparently, only one other study of this kind has ever been reported, that of Kenyon[5] on the acetone photosensitized decomposition of *sec*-butyl chloride in the *vapor phase*.

The dichlorobutane (DCB) compounds selected for this study consist of 1,3-DCB, which typifies the usual head-to-tail structure in PVC, 2,3- and 1,4-DCB, which typify any head-to-head or tail-to-tail microstructural defects in PVC, and 1,2-DCB to round out the group of butyl dichlorides of the non-*gem* type. Further interest attaches to the direct photolysis of these compounds inasmuch as the analogous radiolysis of these compounds was the subject of a prior investigation by Wiley and coworkers.[6] Moreover, the acetone photosensitized formation of HCl from 1,4-DCB was recently reported in a preliminary communication,[7] and further details of this photochemical system, notably the rearrangement to 1,3-DCB, warrant examination at this time.

Work of a related nature which has been published concerns the radiolysis of various propyl[8-11] and butyl[9,12] chlorides and the limited photolysis of *n*-propyl chloride.[8,9]

Experimental Section

The four different DCB's (Aldrich Chemical Co.) were dried for several days with anhydrous Na_2SO_4, then distilled through a Penn State semimicro fractionating column, and the middle 50% fractions were taken for irradiation. Analysis by vpc showed no detectable impurities. Ultraviolet spectra of the DCB's (15 v/v in isooctane, 1-cm cell), run with a Cary Model 14 spectrophotometer, showed absorption commencing at $\sim$2800–2900 Å, and increased to an absorbancy at 2537 Å of 0.040 (1,4-), 0.110 (1,3-), 0.024 (1,2-), and 0.044 (2,3-DCB), and to an absorbancy of 1 at $\leq$2350 Å.

The acetone used in this study was of spectral grade.

Samples of the DCB's, with and without acetone as sensitizer, were sealed at $<10^{-5}$ Torr in tubes with optically flat quartz or Pyrex windows, following several freeze–thaw cycles. The tubes, having an optical path length of 4 mm, were irradiated with 2537- or 3130-Å light at 40° on a merry-go-round unit in a Rayonet Reactor (Southern New England Ultraviolet Co., Middletown, Conn.). The walls of the tubes above the liquid level were covered with aluminum foil to prevent any vapor phase photolysis. The light sources were calibrated with a uranyl oxalate actinometer. The incident intensities at 2537 and at 3130 Å were $\sim 2.32 \times 10^{16}$ and 2.17×10^{16} quanta cm^{-2} sec^{-1}, respectively.

Analysis for HCl evolution (μmol/g neat DCB or total solution) consisted of potentiometric titration with NaOH of methanol–water extracts of the frozen contents of irradiated tubes. Analysis for various organic products was carried out with a 6 ft × 0.25 in. Poropak Q column (He), at 130° for 1 min, then programmed to 230° at 5°/min, the vpc being operated in tandem with a Bendix time-of-flight mass spectrometer. In addition, mass spectra of the residues of irradiated samples, following evaporation of the DCB's and lower molecular weight compounds, were obtained with a Hitachi spectrometer.

Results and Discussion

Direct Photolysis of Dichlorobutanes. The evolution of HCl from neat 1,4- and 1,3-DCB as a function of time of photolysis at 2537 Å is shown in Figure 1. Similar plots were obtained for neat 1,2- and 2,3-DCB, but need not be shown here. The various plots show a decrease in photolysis rate with time of irradiation which resembles the observed decrease in radiolysis rate, with dose, of these DCB's[6] or of n-C_3H_7Cl or n-C_4H_9Cl.[8] This indicates that the decrease in rate of photoproduction of HCl is not attributable to small increases in absorption of the neat DCB's attending uv irradiation;

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[3] W. C. Geddes, *Rubber Chem. Technol.*, **40**, 178 (1967).

[4] M. A. Golub and J. A. Parker, *Makromol. Chem.*, **85**, 6 (1965).

[5] A. S. Kenyon, *J. Amer. Chem. Soc.*, **74**, 3372 (1952); National Bureau of Standards (U. S.) Circular 525, U. S. Government Printing Office, Washington, D. C., 1953, p 81; *Chem. Abstr.*, **48**, 7338*e* (1954).

[6] R. H. Wiley, R. L. S. Patterson, B. Bierbaum, D. J. Parrish, and E. Grünhut, *Conf. Interamer. Radioquim., 1st*, 183 (1963); *Chem. Abstr.*, **64**, 18759*c* (1966).

[7] M. A. Golub, *J. Amer. Chem. Soc.*, **91**, 4925 (1969).

[8] H. L. Benson, Jr., and J. E. Willard, *ibid.*, **83**, 4672 (1961); **88**, 5689 (1966).

[9] M. Takehisa, G. Levey, and J. E. Willard, *ibid.*, **88**, 5694 (1966).

[10] R. E. Johnson and C. E. Miller, Jr., *J. Phys. Chem.*, **63**, 641 (1959).

[11] R. H. Wiley, W. Miller, C. H. Jarboe, Jr., J. R. Harrell, and D. J. Parish, *Radiat. Res.*, **13**, 479 (1960).

[12] E. B. Dismukes and W. S. Wilcox, *ibid.*, **11**, 754 (1959).

Table I. Product Yields in the Direct Photolysis and Radiolysis[a] of Dichlorobutanes

Compound	HCl		Isomers		C_4Cl		Relative yields, 1CB/2CB	
	Φ	G	Φ	G	Φ	G	Φ	G
1,4-DCB	0.032	4.0	0.083[b]	11.13[b]	0.028	2.41	13.6[e]	15.1[i]
1,3-DCB	0.026	4.8	$\lesssim$0.01[c]	2.44[d]	0.019	2.93	1.6[f]	0.82[i]
1,2-DCB	0.097	6.3	$\lesssim$0.01[b]		0.079		1.5[g]	
2,3-DCB	0.089	6.2	$\lesssim$0.01[b]		0.069		0.57[h]	

[a] Reference 6. [b] 1,3-DCB. [c] 2,3-DCB. [d] 2,3-DCB (1.92) + 1,2-DCB (0.52). [e] Consists of 68% 1CB, 5% 2CB, 27% chlorobutenes. [f] Consists of 50% 1CB, 31% 2CB, 19% chlorobutenes. [g] Consists of 40% 1CB, 26% 2CB, 34% chlorobutenes. [h] Consists of 16% 1CB, 28% 2CB, 56% chlorobutenes. [i] Apparently only 1CB and 2CB.

instead, as in the radiolysis case, the downward curvature of the photolysis plot suggests the occurrence of a competing reaction leading to consumption of HCl. From the initial slopes of the photolysis plots, and measured initial absorption properties of the DCB's at 2537 Å, Φ(HCl) values were estimated, and these are compared with corresponding G values in Table I.

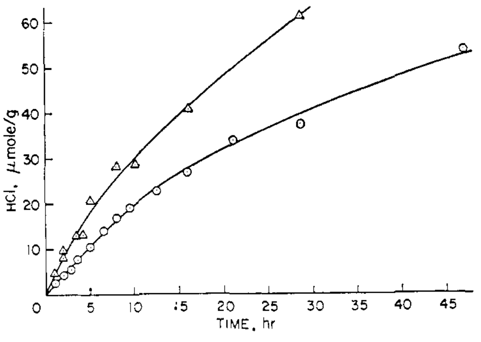

Figure 1. Kinetic plots for photoinduced evolution of HCl from neat 1,4-DCB (○) and 1,3-DCB (△) at 2537 Å.

Qualitatively, it may be noted that the distinctly higher Φ(HCl) values for 1,2- and 2,3-DCB compared to 1,4- and 1,3-DCB find a parallel in the relative magnitudes of the G(HCl) values for these same compounds.

An important reaction accompanying the photoinduced evolution of HCl from neat 1,4-DCB, and one having an even higher quantum yield, is rearrangement to 1,3-DCB, shown in Figure 2. The upward curvature of this plot, analogous to that observed in the radiation-induced isomerization[8,9] of n-C_3H_7Cl to i-C_3H_7Cl and of n-C_4H_9Cl to sec-C_4H_9Cl, has a similar interpretation, *viz.*, some autocatalysis by the HCl produced in the photolysis. Particular significance is ascribed to the ratio of the quantum yields for 1,4 → 1,3 isomerization and HCl evolution, 0.083/0.032, or ~2.6, a ratio which is very close to that for the corresponding G values for 1,4-DCB[6] (11.13/4.0, or ~2.8) (Table I). This factor of 2.6–2.8 can be regarded as a rough measure of the chain length of the isomerization in the early stages of the photolysis (or radiolysis) of the neat 1,4-DCB. Interestingly, a similar ratio of quantum yields (~2.8) for the photoinduced isomerization and evolution of HCl at ~2200 Å in the case of n-C_3H_7Cl can be inferred from the work of Benson and Willard,[8] although the quantum yields for these reactions could not be individually determined. At the end of the present study, it was observed that irradiation of an especially "clean" sample of neat 1,4-DCB (absorption commencing at ~2500 Å) resulted in a similar chain length for the 1,4 → 1,3 isomerization, but as in the Benson and Willard investigation the individual quantum yields for rearrangement and HCl evolution could not be determined.

In contrast to the moderately efficient photoinduced 1,4 → 1,3 rearrangement, there was no evidence for the reverse rearrangement in the case of 1,3-DCB. This is in keeping with the failure of i-C_3H_7Cl to rearrange to n-C_3H_7Cl, or of sec-C_4H_9Cl to rearrange to n-C_4H_9Cl, on exposure to uv or ionizing radiation.[9,11,12] However, 1,3-DCB does undergo a minor photorearrangement to 2,3-DCB but, unlike the corresponding radiolysis, showed no formation of 1,2-DCB. Evidence was also obtained for a minor photoinduced rearrangement in 1,2- and 2,3-DCB to 1,3-DCB, but data on the analogous radiation-induced reactions are not available.

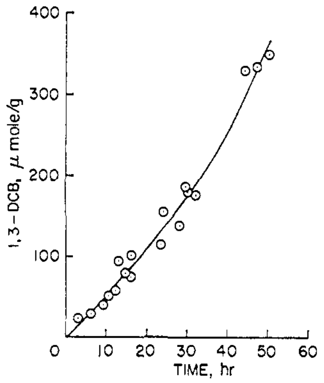

Figure 2. Kinetic plot for 1,4 → 1,3 photorearrangement of neat 1,4-DCB at 2537 Å.

Table I also presents comparative yields of C_4Cl products formed in the photolysis and radiolysis of the various DCB's. These products comprise 1-chlorobutane (1CB), 2-chlorobutane (2CB), and various unspecified chlorobutenes. Although these compounds could not be adequately separated by vpc, their presence could nevertheless be verified, and their relative amounts estimated, by combined vpc–mass spectral analysis. The radiolysis study[6] did not disclose any data on chlorobutene formation, but a small amount of this product could be expected by analogy to the indicated formation of propylene in low yield in the radiolysis of n-C_3H_7Cl.[8] It is noteworthy that the ratio of quantum yields for 1CB and 2CB formation from 1,4-DCB is comparable to the ratio of corresponding G values; the agreement between the respective ratios in the case of 1,3-DCB is not as good (Table I). The ratios of yields of 1CB and 2CB decrease in the series 1,4- to 2,3-DCB, in the manner expected from their structures.

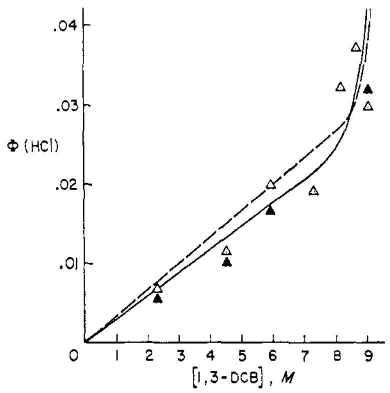

Figure 3. Quantum yield for HCl evolution from 1,3-DCB–acetone solutions at 3130 Å. The open triangles denote runs in quartz tubes and the closed triangles denote those in Pyrex. The dotted line represents prior data for 1,4-DCB–acetone solutions.[7]

Finally, it should be noted that, in analogy to the formation of dichloro- and monochlorohexanes in the photolysis of n-C$_3$H$_7$Cl,[8] definite evidence was obtained for the formation of tetrachloro- and trichlorooctanes in the residues of uv-irradiated DCB's. On the other hand, dichlorooctanes, which would be the counterpart of n-hexane formed in the n-C$_3$H$_7$Cl case, could not be detected in the DCB case. Qualitatively, the yield of tetrachlorooctanes, though small, was considerably larger than that of trichlorooctanes, in line with the relative yields of their di- and monochlorohexane counterparts.

Acetone Sensitized Photolysis of Dichlorobutanes. Figure 3 shows the concentration dependence of quantum yield for acetone sensitized evolution of HCl from 1,3-DCB at 3130 Å, along with a previously reported plot[7] for 1,4-DCB–acetone solutions. Evidently, the two different DCB's are about equally efficient in removing excitational energy from acetone and in undergoing sensitized decomposition. The somewhat lower plot for 1,3-DCB probably reflects the somewhat lower Φ(HCl) for direct photolysis of this compound compared to 1,4-DCB (Table I). The initial *sensitized* Φ(HCl) values ($\lesssim 1\%$ photolysis) from 1,3-DCB reported in the figure, in those runs using quartz tubes, represent only the energy transfer contribution after subtracting the calculated contribution due to direct absorption by 1,3-DCB at 2537 Å (there being about 15% emission of this line in the 3130-Å source). It is evidently immaterial whether the system is irradiated above or below 3000 Å so long as the radiation lies within the broad acetone n → π^* band. This accords well with what is known about the photolysis of neat liquid acetone at 2537 and at 2800–3300 Å.[13]

The approximate linearity of the 1,3-DCB plot (Figure 3) over a rather wide range of substrate concentrations, as well as the sharp upturn at [1,3-DCB] $\sim$ 9 M ([acetone] $\lesssim$ 0.2 M), can be interpreted on the same basis as that proposed earlier for 1,4-DCB–acetone solutions,[7] *i.e.*, sensitization by the *monomer* form of the $[\text{n},\pi^*]^1$ state of acetone. In the region of very high acetone dilution, the concentration of the monomer form (in equilibrium with the excimer), and hence Φ(HCl), decreases sharply with increase in acetone concentration, while at all other acetone concentrations

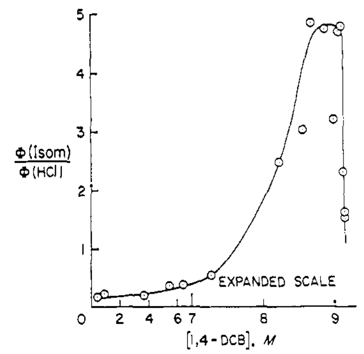

Figure 4. Relative quantum yields for sensitized 1,4 → 1,3 rearrangement and HCl evolution in 1,4-DCB–acetone solutions at 3130 Å.

($\gtrsim$0.1 M) the $[\text{n},\pi^*]^1$ state exists mainly in the *excimer* form, and the photolysis rate is then linearly dependent on the DCB concentration.[13a]

Similar sensitization results were obtained for acetone solutions of 1,2- and 2,3-DCB, but these need not be presented here.

Just as in the direct photolysis of 1,4-DCB, 1,4 → 1,3 rearrangement accompanies HCl evolution in the acetone sensitized photolysis. Figure 4 shows that the ratio, Φ(isom)/Φ(HCl), is quite dependent on the 1,4-DCB concentration in acetone. Over the entire range of concentrations, where acetone $[\text{n},\pi^*]^1$ states would be mainly in the excimer form (*i.e.*, [DCB] $\lesssim$ 9 M), there is a steady decrease in chain length from $\sim$4.8 to $\sim$0.2 with increasing dilution of DCB by acetone. At [DCB] $\gtrsim$ 9 M, where the $[\text{n},\pi^*]^1$ state could exist largely in the monomer form, there is again a rather sharp drop in the chain length, this time to values below the chain length observed in the direct photolysis of neat 1,4-DCB ($\sim$2.6; see above).

Mechanism. The direct and sensitized photolyses of 1,4-DCB leading to evolution of HCl and isomerization to 1,3-DCB can be depicted by the following elementary steps, analogous to those proposed for the radiolysis of DCB's[6] or the photolysis and radiolysis of n-C$_3$H$_7$Cl.[8,11]

$$\text{ClCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl} \xrightarrow[\text{acetone)}]{\text{uv (alone or with}} \text{ClCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\cdot + \text{Cl}\cdot \tag{1}$$

$$\text{ClCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl} + \text{Cl}\cdot \longrightarrow \text{ClCH}_2\text{CH}_2\dot{\text{C}}\text{HCH}_2\text{Cl} + \text{HCl} \tag{2}$$

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(13) R. Pieck and E. W. R. Steacie, *Can. J. Chem.*, **33**, 1304 (1955).

(13a) NOTE ADDED IN PROOF. G. D. Renkes and F. S. Wettack, *J. Amer. Chem. Soc.*, **91**, 7514 (1969), very recently demonstrated that, contrary to the report of M. O'Sullivan and A. C. Testa, *ibid.*, **90**, 6245 (1968), acetone and other aliphatic ketones do not exhibit *both* monomer and excimer fluorescence but only a single (monomer) peak at 405 nm characteristic of the $[\text{n},\pi^*]^1$ state. An impurity present in the ketones employed by the latter workers was apparently responsible for the fluorescence they observed at 345 nm, a peak which was quenched at sufficiently high ($>10^{-2}$ M) ketone concentration. Whatever the nature of this impurity, it was evidently also present in our sample of acetone[7] as well as in a sample of diethyl ketone examined by other workers [J. C. W. Chien and W. P. Conner, *ibid.*, **90**, 1001 (1968)]. Whether such an impurity is the cause for the sharp upturn in Φ(HCl) at very high DCB concentration (Figure 3) or very low acetone concentration (Figure 2 in ref 7) is open to question at this time, and further work will be undertaken to settle this point. However, the contribution of the impurity to the acetone-sensitized evolution of HCl from DCB should be negligible over the wide range of substrate concentrations (0 to $\sim$8.5 M) in which the Φ(HCl)–[DCB] plot is approximately linear. Elsewhere in the text, reference to the acetone *excimer* state should thus be reinterpreted as the monomer state, while the effects attributed to the *monomer* state remain to be accounted for.

$$\mathrm{ClCH_2CH_2\dot{C}HCH_2Cl} \rightleftarrows \mathrm{ClCH_2CH_2CHClCH_2\cdot} \qquad (3)$$

$$\mathrm{ClCH_2CH_2CHClCH_2\cdot} + \mathrm{C_4H_8Cl_2} \longrightarrow \mathrm{ClCH_2CH_2CHClCH_3} + \mathrm{ClCH_2CH_2\dot{C}HCH_2Cl} \qquad (4)$$

$$\mathrm{ClCH_2CH_2CHClCH_2\cdot} + \mathrm{HCl} \longrightarrow \mathrm{ClCH_2CH_2CHClCH_3} + \mathrm{Cl\cdot} \qquad (5)$$

To the extent that step 4 and/or 5 can compete with radical–radical recombination processes, such as step 6 leading to the observed tetrachlorooctanes, the isomerization will be a chain reaction capable of exhibiting some HCl catalysis (see Figure 2). The chain length of the process will be given roughly by the Φ(isom)/Φ(HCl) ratio. That this ratio for neat 1,4-DCB is practically the same as the corresponding ratio of *G* values, as noted earlier, indicates that the photolysis and radiolysis mechanisms are virtually alike. Insofar as the formation of HCl and 1,3-DCB is concerned, the role of ionic species and hot radicals in the radiolysis case can be disregarded.

$$2\mathrm{C_4H_7Cl_2\cdot} \longrightarrow \mathrm{C_8H_{14}Cl_4} \qquad (6)$$

In terms of the above mechanism, the observed chlorobutanes are formed through abstraction of hydrogen from 1,4-DCB by the $\mathrm{C_4H_8Cl\cdot}$ radical generated in step 1. Chlorobutenes, on the other hand, presumably arise from occasional molecular elimination of HCl from an excited DCB molecule.

On replacement of 1,4-DCB by 1,3-, 1,2-, or 2,3-DCB in step 2, and with appropriate substitutions in steps 3–5, the above mechanism can account for the observed photorearrangements in the latter three DCB's. However, since the Cl atom produced in step 1 abstracts an H atom from a secondary carbon atom in preference to one on a primary carbon,[9] there is negligible 1,3 → 1,4 isomerization, but some 1,3 → 2,3 rearrangement. Likewise, there is some 1,2 → 1,3, and some 2,3 → 1,3 rearrangement.

At the very low HCl concentration prevailing in the initial stages of the 1,4-DCB photolysis, step 4 competes with step 5 as a route to 1,3-DCB. As the HCl content slowly increases during the irradiation, step 5 becomes progressively more important and contributes an autocatalytic effect which, superimposed on the effects of step 4, causes a slight upward curvature in the kinetic plot for 1,3-DCB formation (Figure 2). An analogous situation was encountered in the radiation-induced isomerization of *n*-$\mathrm{C_4H_9Cl}$ to *sec*-$\mathrm{C_4H_9Cl}$[9] where an *initial G* value was attributed to a process *not* dependent on the growth of HCl concentration; however, with increase in HCl concentration during irradiation, or by incorporation of known amounts of HCl prior to irradiation, marked HCl catalysis occurred along with substantial increases in yield of *sec*-$\mathrm{C_4H_9Cl}$. The parallelism between the photorearrangement of 1,4-DCB and the radiation-induced rearrangement of *n*-$\mathrm{C_4H_9Cl}$ is reinforced by the fact that the *G*(isom)/*G*(HCl) ratio for the latter system (at an average HCl concentration during irradiation of ∼0.125 mole %) is ∼2.3 (estimated from Figure 3 in ref 9), whereas the initial Φ(isom)/Φ(HCl) ratio for the DCB system (corresponding to the same average HCl concentration) is ∼2.6, as noted earlier.

The reasonableness of the above mechanism can be seen in a semiquantitative consideration of the pertinent rate constants. Step 2, which is much faster than either step 4 or 5, is estimated[14] to have a constant, k_2, of $\sim 10^{10.3-0.3/\theta}$ or $\sim 10^{10.1}\ M^{-1}\ \mathrm{sec}^{-1}$ at room temperature [$\theta = 2.3RT$ kcal/mol]. The rate constant for step 4 is estimated[15] as $k_4 \sim 10^{8-10/\theta}\ M^{-1}\ \mathrm{sec}^{-1}$, while that for step 5 is assumed[16] to be $k_5 \sim 10^{8-6/\theta}\ M^{-1}\ \mathrm{sec}^{-1}$. Thus, at the very low HCl concentration mentioned above

$$\frac{\text{rate of step 4}}{\text{rate of step 5}} = \frac{k_4[\text{1,4-DCB}]}{k_5[\text{HCl}]} \sim \frac{10^{8-10/\theta}}{10^{8-6/\theta}}(800) \sim 1$$

a relation which supports the notion that the rate-controlling steps 4 and 5 are indeed competitive under the conditions existing in the photolysis of 1,4-DCB.

In the case of acetone photosensitization, the marked diminution in Φ(isom)/Φ(HCl) at [1,4-DCB] < 8.6 *M* (Figure 4) can be ascribed mainly to the increasing likelihood that hydrogen abstraction by chlorine atoms will involve acetone instead of DCB. Abstraction from acetone has the effect of producing HCl without yielding, at the same time, the radical precursor to 1,3-DCB. On the other hand, the sharp drop in Φ(isom)/Φ(HCl) at [1,4-DCB] > 9 *M* is not so readily explained. It is conceivable that in this concentration range collisional deactivation by DCB will involve mainly acetone [n,π*][1] monomer states *just prior to excimer formation*, whereas at lower DCB (or higher acetone) concentrations the monomer states involved would be those formed on excimer dissociation, and possibly possessing lower available energy than the instantaneously formed singlet states. If this is so, there could be a somewhat higher yield of molecular detachment of HCl relative to C–Cl rupture (step 1), and hence lower Φ(isom)/Φ(HCl), in case of sensitization by nascent excited monomer states than in the case of sensitization by monomer states resulting from excimer dissociation.

A minor product formed in the DCB–acetone photolysis system is mesityl oxide, the relative amount of which increases with increasing acetone content. This product, the result of an acetone condensation reaction, has a negligible effect, at the low levels at which it is formed, on the quantum yields obtained. This was confirmed by carrying out DCB–acetone runs with very small amounts of mesityl oxide added prior to irradiation. Apart from mesityl oxide, no other detectable products stemming from photolysis of acetone were encountered in the uv irradiation of acetone solutions of DCB. This indicates that methyl radicals are not involved in the mechanism for the acetone-sensitized photoproduction of HCl in the liquid state. This is altogether different from the situation in the vapor phase irradiation of *sec*-butyl chloride in the presence of acetone, reported by Kenyon.[5] Here the ketone undergoes extensive type I photodissociation, and the HCl is produced from thermal decomposition of unstable compounds formed in secondary reactions

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(14) See G. C. Fettis and J. H. Knox in "Progress in Reaction Kinetics," Vol. 2, G. Porter, Ed., The Macmillan Co., New York, N. Y., 1964, for the process $\mathrm{ClCH_2CH_2CH_2CH_3} + \mathrm{Cl\cdot} \rightarrow \mathrm{ClCH_2\dot{C}HCH_2CH_3} + \mathrm{HCl}$.

(15) A. F. Trotman-Dickenson and G. S. Milne, "Tables of Bimolecular Gas Reactions," NSRDS–NBS 9, U. S. Government Printing Office, Washington, D. C., 1967, p 71.

(16) According to S. W. Benson, "Thermochemical Kinetics," John Wiley & Sons, Inc., New York, N. Y., 1968, p 159, the activation energy for $\mathrm{R\cdot} + \mathrm{HCl} \rightarrow \mathrm{RH} + \mathrm{Cl\cdot}$ should be 1 kcal/mol in excess of the endothermicity, or in this case ∼6 kcal/mol.

involving various radicals arising from the butyl chloride and acetone.

Comparison with Polyvinyl Chloride. It is interesting to compare the Φ(HCl) and *G*(HCl) values for 1,3-DCB (Table I) with corresponding data in the literature for pure PVC films. The relevant data for this comparison are those of Miller[17] who obtained *G*(HCl) = 13 for the electron irradiation of PVC *in vacuo* at 30°, and those of Petit and Zaitoun[18] who obtained Φ(HCl) = 0.13 for the uv irradiation at 3023 Å of PVC films *in air*. Since it has been shown[19] that the *G*(HCl) for irradiation of PVC in air is ∼2.3 times the *G* value for irradiation under vacuum, a value of 0.13/2.3, or 0.057, might be indicated for Φ(HCl) for PVC *in vacuo*. On this basis, we notice a striking similarity between the ratio of *G*(HCl) values for vacuum irradiation of PVC and its likely model compound, 1,3-DCB (13/4.8, or ∼2.7), and the corresponding ratio of Φ(HCl) values (0.057/0.026, or ∼2.2). A similar correlation was noted previously connecting the photo- and radiation-induced production of unsaturation (due to HCl elimination) in PVC containing residual ketonic solvent with corresponding results for solvent-free PVC.[4]

In view of the correlation between 1,3-DCB and PVC noted in this study, the Φ(HCl) ∼ 0.01 recently reported by Reinisch and Gloria[20] for PVC irradiation at 2537 Å appears quite low. These workers previously reported[21] an initial Φ(HCl) ∼0.06–0.10 for polychromatic irradiation of PVC which decreased to ∼0.02–0.03 after extended irradiation. Further work on the photolysis of PVC and other model compounds should help to clarify this question of quantum yields.

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(17) A. A. Miller, *J. Phys. Chem.*, **63**, 1755 (1959).

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On the Inherent Optical Activity of Organic Disulfides

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Abstract: A consideration of the simple Bergson model and a semiempirical CNDO calculation lead to a natural explanation of the lack of inherent optical activity of the first uv transition in open-chain disulfides and strong inherent activity in cyclic disulfides. Inherent activity of sign opposite to the latter is predicted for the so-far hypothetical disulfides with dihedral angles considerably larger than 90°. Matrix elements of the angular momentum operator were calculated in a simple way from resonance integrals; this procedure might be of general interest in semiempirical methods.

A thorough understanding of the relation between stereochemistry and circular dichroism (CD) of disulfides would be helpful in investigations of the conformation of numerous biologically important compounds.[2,3] The first step in this direction was made when the antibiotic gliotoxin, with a negative first band in the CD spectrum, was found to have left-handed chirality at the disulfide linkage.[4] From an investigation on 1,2-dithianes with known absolute configuration, Carmack and Neubert formulated the following rule[5]: six-membered ring systems with the disulfide chromophore twisted in the sense of a left-handed helix have first uv transitions of negative rotatory strength (at 280–290 mμ). The rotatory strength is quite high (∼−0.2 × 10^{-38} cgs unit), typical of "inherently dissymmetrical" chromophores. The authors cautioned against indiscriminate use of the rule for rings of different size and open-chain disulfides until more is known about effects of perturbations due to asymmetry of the environment. The second uv band (at 240 mμ) gives a CD band of sign opposite to the first band; however, its dichroism is more sensitive to minor perturbations (solvent, etc.), and the authors do not recommend it for diagnostic purposes.[5]

Similar conclusions concerning the optical activity of 1,2-dithianes were independently reached by Dodson and Nelson,[6] and by Claeson,[7] who pointed out that the observed optical activity is due to inherent dissymmetry of the chromophore, which usually greatly outweighs effects due to environmental perturbations, so that the rule should be applicable to disulfides in general. However, he also noted that the magnitude of the inherent optical activity must depend on the dihedral angle *ϕ*, since for *ϕ* = 0 or 180°, the chromophore is planar and thus inherently inactive, and suggested that in instances of low inherent activity, the effects of peripheral asymmetry may become dominant. Bey-

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