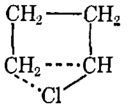
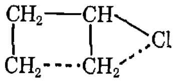
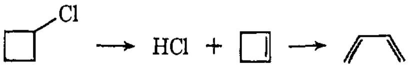
We think it is unlikely that the difference in stabilities between I and II is appreciably more than 2 kcal mole^{-1}, but even a figure as small as this would ensure that I was very much the more important species in determining the Arrhenius parameters for the decomposition. This would explain the reduction in the energy of activation for this reaction compared with cyclobutane. The lowered A factor must come from a tightening of the transition complex and is probably to be associated with the loss of entropy of internal rotations again as compared with the cyclobutane activated complex. This cannot be simply due to an increase in the barrier to internal rotation of the type as occurs in going from ethane to ethyl chloride, since such an effect would be far too small. We suggest it arises from a structure involving a chlorine bridge. Such a complex is shown in Ia. Alternatively, if in fact the stabilization by the chlorine substitution is appreciably less than 2 kcal mol^{-1}, then II must be seriously considered, and it then follows that IIa might be a reasonable representation of the transition complex. It should be noted that a chlorine bridge of the type shown in IIa has been proposed in the transition complex for the isomerization of chlorocyclopropane,[4] though in this case chlorine migration occurs.


Ia


IIa

The reaction leading to the elimination of hydrogen chloride has a "normal" A factor which is typical of such eliminations from open-chain alkyl chlorides. The activation energy is, however, higher than for 2-butyl chloride (50.1 kcal mol^{-1}) and also for cyclohexyl and cyclopentyl chlorides (49.2 and 48.3 kcal mol^{-1}, respectively). This must be attributed to the greater strain involved in bringing the chlorine and hydrogen to the transition-state configuration. On the basis of the analytical data alone, it is not possible to distinguish between the direct formation of butadiene as depicted in eq 2 or a two-stage process involving the intermediate formation of cyclobutene as shown in eq 3. Since the HCl elimination will be favored by a reduction in the carbon–carbon bond involved, it appears unlikely on energetic grounds that the reaction yields butadiene directly and we favor (3).


(3)

It is interesting to note that while the concerted *cis* elimination of HCl from alkyl chlorides and alicyclic chlorides is an orbital symmetry-forbidden process,[11] the one-step formation of butadiene and HCl would be a symmetry-allowed process. If such considerations were of importance in controlling the energetics of these eliminations, then it would have been anticipated that in the present study this reaction would have had an appreciably lower energy of activation than that observed in the case of cyclopentyl chloride. It is possible that the approximation of treating the σ C–Cl bond as equivalent to the σ C–H bond when constructing the appropriate MO which is inherent in the orbital symmetry arguments is at the bottom of this unexpected finding. An alternative statement of this suggestion is that the differences between these bonds is so marked that the molecular orbitals are not appreciably delocalized, and delocalized molecular orbitals are required (indeed are inherent) in the application of the orbital symmetry arguments.

Acknowledgment. We thank Dr. W. G. Rothschild for a sample of chlorocyclobutane. We also thank the SRC for the award of a research studentship to A. T. C.

---

(11) R. B. Woodward and R. Hoffmann, *Angew. Chem.*, in press.

Vibrational Effects in the Xylenes[1]

W. Albert Noyes, Jr., and D. A. Harter

Contribution from the Chemistry Division, Argonne National Laboratory, Argonne, Illinois 60439.
Received May 29, 1969

Abstract: An increase in pressure of inert gas enhances the fluorescences of the xylenes when exposed to radiation of shorter wavelengths than the 0,0 bands. At longer wavelengths the reverse effect is noted. An increase in temperature causes a decrease in fluorescence. Quantum yields of isomerization of xylenes to each other are wavelength dependent and are very small near the 0,0 band. These yields increase slightly with increase in temperature. 1,3-Pentadiene effectively quenches the singlet states of the xylenes. A mechanism can be advanced which correlates these various facts.

It is recognized that when light emission from an excited molecule is competitive with some other process whose rate increases with increase in vibrational level there may be enhancement of fluorescence with increase in total pressure.[2-4] The competing processes may be hard to elucidate but could include dissociation, isomerization, and intersystem cross-over to a state of different multiplicity.

---

(1) Published with the permission of the Atomic Energy Commission.

(2) F. C. Henriques, Jr., and W. A. Noyes, Jr., *J. Am. Chem. Soc.*, **62**, 1038 (1940).

(3) G. M. Almy and S. Anderson, *J. Chem. Phys.*, **8**, 805 (1940).

(4) C. S. Burton and W. A. Noyes, Jr., *ibid.*, **49**, 1705 (1968).

The present work concerns mainly the fluorescent efficiencies of the three xylenes, but isomerization and intersystem cross-over will be mentioned briefly.

Experimental Section

Fluorescent yields of the three xylenes in the gas phase were obtained relative to the yield of benzene. The latter at room temperature is assumed to have the value 0.18 at 2530 Å.[5]

A T-shaped cell 4.0 cm in length with a side arm 2.2 cm in diameter and 3.8 cm in length was used. With a cell of this dimension, "round-the-corner" corrections are reduced.

Incident light was obtained with one of several high-pressure xenon lamps, although high-pressure xenon mercury lamps were used for certain wavelengths. Monochromatic light was obtained with a Bausch and Lomb No. 33-86-45 monochromator with a dispersion of 16 Å mm^{-1}. In nearly all the work 2-mm entrance and exit slits were used. The fraction of the light absorbed was obtained by use of a RCA 935 phototube in conjunction with a Keithley picoammeter. Since this tube has a slight change in sensitivity with wavelength, corrections were obtained by use of a sodium salicylate layer.[6] Corrections were as follows: 2400 Å, 0.770; 2480 Å, 0.763; 2530 Å, 0.756; 2590 Å, 0.747; 2720 ± 20 Å, 0.727 (the coefficients are the numbers by which the apparent value of the light absorbed must be divided to bring the ammeter readings to relative numbers of photons absorbed per second).

The fluorescent light was passed through a Bausch and Lomb No. 35-86-01 monochromator with 2-mm slits and measured with a 1P28 photomultiplier tube in connection with a picoammeter. Measurements were tried with several intervals of monochromator setting and the integrated areas under the curves of wavelength *vs.* current obtained. It appeared that with 50-Å intervals, except near the peak where more frequent settings were necessary, the area did not differ more than the experimental error from that obtained with closer settings. Indeed, at a distance of about 200 Å on the long-wavelength side from the absorption maximum, readings every 100 Å proved ample.

The procedure was to measure the arbitrary fluorescent efficiency of benzene in terms of integrated microamperes due to emitted light divided by integrated microamperes due to absorbed light. Call this $Q_B{}^0$. The same thing was then done for the xylene. Call this $Q_X{}^0$. The absolute fluorescent efficiency of the xylene is given by

$$0.18(Q_X{}^0/Q_B{}^0) = Q_X \qquad (1)$$

Both $Q_X{}^0$ and $Q_B{}^0$ contain the corrections listed above for the 935 tube. It is recognized that the sensitivity of the 1P28 varies with wavelength and that distributions of emitted intensities with wavelength are not identical for the various molecules studied. However, a semiempirical calculation of emission efficiencies corrected for variation of sensitivity with wavelength showed this error to be small compared to others.

Mixing of the xylenes with added gases proved to be a serious problem. However, the mixtures were prepared at the end in a large bulb with an insert finger into which liquid nitrogen could be poured. Evaporation from this kind of a surface inside a large bulb proved to give reasonably satisfactory mixing.

The constancy of the light source was one of the chief sources of error, but this was monitored as well as possible by running $Q_B{}^0$ at intervals.

Triplet-state yields were determined by the method of Cundall.[7] A column of silver nitrate on Chromosorb, 6.5 ft in length, at 50° was used to determine *cis-* and *trans*-butene-2. Measurements were made both by starting with the *cis* and starting with *trans* compound. Results at the long wavelengths around 2600–2700 Å seemed reasonably satisfactory, but results at shorter wavelengths showed inconsistencies and will not be presented. The reasons for this behavior were not apparent.

Isomerization yields as well as attempts to locate other products such as toluene, ethylbenzene, and methylethylbenzene as well as lighter molecules were made by vapor-phase chromatography using a column of 5% Bentone 34; 5% diisodecyl phthalate on Chromosorb, 6 ft in length at 70°; and for the latter, molecular sieve 13×, 12 ft in length at room temperature. The light intensities transmitted were measured by the ferrioxalate actinometer.[8] Corrections were made for the absorption by the rear window of the cell and the window of the actinometer vessel.

Temperature could be varied by a block furnace which has already been described.[9]

Added gases studied were butane, cyclohexane, and *cis*-butene-2. These were all Phillips Research Grade and purified by outgassing.

The xylenes were all Phillips Research Grade and were purified by fractional distillation at low pressures.

The fluorescence measurements finally reported were all made in a mercury-free, grease-free line equipped with metal values from Autoclave Engineers, Inc., Erie, Pa., or Hoke Inc., Cresskill, N. J., and evacuated with an Eck and Krebs oil diffusion pump.

Results

(a) Fluorescence. Tables I–III summarize fluorescent quantum yields for the three xylenes. Literally hundreds of determinations were made and the values are read from smooth curves. Cyclohexane, *cis*-butene-2, and butane all showed about the same effect on fluorescent efficiency, but the vast majority of the results were obtained with added butane.

Table I. Fluorescent Efficiencies of *o*-Xylene (2–5 Torr)

Total pressure, Torr	Temp, °C	2400 Å	2480 Å	2530 Å	2590 Å	2710 Å
0	25 ± 2	0.015	0.13	0.29	0.36	0.38
50		0.056	0.22	0.32	0.36	0.37
100		0.080	0.25	0.33	0.34	0.32
200		0.11	0.28	0.34	0.38	0.30
400		0.16	0.31	0.34	0.38	0.30
100 (Xe)		0.055	0.17	0.23	0.28	0.27
360 (He)		0.03	0.23	0.025	0.37	0.33
360 (Ar)		0.07	0.19	0.31	0.35	0.34
0	61	0.01	0.10	0.19	0.30	0.35
100		0.11	0.13	0.19	0.22	0.24
400		0.14	0.17	0.18	0.21	0.21
0	114	0.006			0.21	0.29
100		0.005	0.05 av	0.09 av	0.14	0.18
400		0.022			0.10	0.10
100 (Xe)		0.01	0.05	0.11	0.17	0.22
360 (He)		0.02	0.07	0.12	0.17	0.26
360 (Ar)		0.01	0.05	0.10	0.14	0.15

Table II. Fluorescent Efficiencies of *m*-Xylene (2–5 Torr)

Total pressure, Torr	Temp, °C	2400 Å	2480 Å	2530 Å	2590 Å	2725 Å
0	25 ± 2	0.01	0.04	0.15		0.35
50		0.03	0.12	0.22		0.31
100		0.06	0.15	0.23	0.30 av	0.30
200		0.09	0.18	0.25		0.29
400		0.11	0.22	0.28		0.28
360 (He)		0.04	0.16	0.23	0.33	0.31
360 (Ar)		0.01	0.10	0.17	0.23	0.25
100 (Xe)		0.07	0.09	0.16	0.12	0.27
0	61	0.02	0.04	0.11	0.24	0.32
100		0.03	0.08	0.15	0.20	0.21
400		0.03	0.14	0.14	0.16	0.19
0	114		0.015	0.067	0.15	0.26
100		0.01 av	0.022	0.060	0.10	0.15
400			0.035	0.054	0.08	0.10
100 (Xe)		0.00	0.005	0.055	0.12	0.23
380 (He)		0.003	0.023	0.058	0.12	0.20
370 (Ar)		0.03	0.032	0.065	0.11	0.17

---

(5) W. A. Noyes, Jr., W. A. Mulac, and D. A. Harter, *J. Chem. Phys.*, **44**, 2100 (1966).

(6) K. J. Nygaard, *J. Opt. Soc. Am.*, **55**, 944 (1965).

(7) R. B. Cundall and T. F. Palmer, *Trans. Faraday Soc.*, **56**, 1211 (1960).

(8) J. H. Baxendale and N. K. Bridge, *J. Phys. Chem.*, **59**, 783 (1955).

(9) W. A. Noyes, Jr., W. A. Mulac, and M. S. Matheson, *J. Chem. Phys.*, **36**, 880 (1962).

Table III. Fluorescent Efficiencies of *p*-Xylene (2–5 Torr)

Total pressure, Torr	Temp, °C	2400 Å	2480 Å	2530 Å	2590 Å	2740 Å
0	26 ± 2	0.06	0.22	0.36	0.44	0.52
100		0.22	0.37	0.49	0.48	0.45
400		0.34	0.50	0.50	0.48	0.44
100 (Xe)		0.14	0.20	0.31	0.32	0.31
370 (He)		0.12	0.37	0.47	0.51	0.43
370 (Ar)		0.24	0.37	0.49	0.47	0.46
0	61	0.04	0.16	0.28	0.39	0.44
100		0.20	0.34	0.42	0.44	0.41
400		0.30	0.43	0.46	0.42	0.37
0	114	0.04	0.10	0.19	0.32	0.42
100		0.08	0.16	0.24	0.30	0.31
400		0.12	0.25	0.23	0.29	0.28
100 (Xe)		0.01	0.07	0.19	0.26	0.31
370 (He)		0.08	0.18	0.29	0.36	0.39
370 (Ar)		0.03	0.12	0.23	0.26	0.34

(b) Isomerization. Quantum yields of isomerization of the three xylenes have been determined but will not be reported in detail here for the following reasons.

It has been shown by Wilzbach and Kaplan that the photochemical transformation of one xylene to another probably proceeds through an intermediate such as dimethylbenzvalene.[10] This intermediate may in some instances be unstable thermally, and in some instances also photochemically. It may revert to the xylene from which it was formed or give a new xylene. In some instances it may give products which are not xylenes. Thus where I is an intermediate

$$X^o + h\nu = I \tag{2}$$

and X^o is, for example, *o*-xylene. If thermal reaction follows

$$I = X^o \tag{3}$$

$$= X^m \tag{4}$$

where X^m is *m*-xylene. Thus

$$+\frac{d(X^m)}{dt} = k_4(I) = \frac{k_4 I_a}{k_3 + k_4} \tag{5}$$

where I_a is the number of photons absorbed per unit volume per second. At present there is no valid way to determine $k_4/(k_3 + k_4)$. If $k_3 = k_4$ the true yield for energy balancing purposes would be $2\Phi(X^m)$.

If, on the other hand, I disappears photochemically to give X^o and X^m, one has

$$I + h\nu = X^o \qquad I_a' \tag{6}$$

$$= X^m \qquad I_a'' \tag{7}$$

The amount of light absorbed by I will depend on its concentration. Actually the same wavelengths may not cause both (6) and (7) so that the problem could be extremely complex. If I disappears only by (6) and (7), its concentration at any time will be

$$(I) = \int_0^t I_a\,dt - \int_0^t I_a'dt - \int_0^t I_a''dt \tag{8}$$

Since the three xylenes absorb in the same wavelength region, the first integral must be corrected for absorption by *m*-xylene. This could be neglected in the runs performed. However, in the absence of more information than now exists about dimethylbenzvalenes and other isomers of the xylenes, it is impossible to evaluate the second and third integrals. The possibility of dimethylfulvene as an intermediate would further complicate matters since its behavior in giving xylene isomers is unknown.

The possibility exists, therefore, that absorption of one photon would be required to produce I and $1/\alpha$ photons to cause I to give *m*-xylene where α is the fraction of I which goes to *m*- rather than to *o*-xylene. For energy-balancing purposes, the yield for (2) may be several times the net yield of *m*-xylene.

One further possibility should be kept in mind as this matter is studied further: there may be a xylene-sensitized disappearance of I.

We will summarize briefly the isomerization data. (1) *o*-Xylene gives only *m*-xylene unless runs are very long and the *m*-xylene concentration is allowed to build up. Φ_{X^m} varies from 0.025 at 2480 Å to 0.000 at 2710 Å at 1 Torr and 26°. It decreases to about 0.009 at 2480 Å with 283 Torr of butane and is not more than 0.002 at 2710 Å under these conditions. At 114° yields change little with pressure but are less at long wavelengths.

(2) *m*-Xylene gives both *o*-xylene and *p*-xylene. $\Phi_{X^o} = 0.002$ and $\Phi_{X^p} = 0.038$ (1 Torr, 2480 Å, 26°). As the wavelength increases the yield of the *para* decreases more rapidly than that of the *ortho* compound. The effect of pressure seems to be greater on the yield of *o*-xylene than on the yield of *p*-xylene. At 114° the yields change little except possibly they may be slightly greater than they are at 25° at 2725 Å.

(3) *p*-Xylene might be expected to give only *m*-xylene, and this seems to be true. However, the analysis for *m*-xylene is less satisfactory in the presence of much *p*-xylene than the reverse. In any case, all isomerization yields of *p*-xylene are low, and the same trend with wavelength is observed as for the others.

For reasons given above, the primary yield of (2) may not be calculated from these data. It is almost certain that it decreases at long wavelengths and at high pressures and that even under the most favorable conditions at 2400 and 2480 Å it does not exceed about 0.2. It is essentially zero at 2590 and at 2700–40 Å under all conditions for all three xylenes. Thus, vibrational relaxation reduces the formation of isomers.

(c) Triplet-State Yields. Since added gases cause vibrational relaxation, there is no way to determine triplet-state yields as they would have been without added gases. This is not, however, the only cause for difficulty, and our results with the Cundall method[5] are not satisfactory, particularly at short wavelengths. We have not been able to discover the reason for this. The triplet yield of *o*-xylene at 2550–2710 Å at 5 Torr plus 54 Torr of *cis*-butene-2 seems to be about 0.63 ± 0.04. Thus, within experimental error at the long-wavelength end of the region studied, the sum of fluorescent- and triplet-state yields is unity. It is safe to say that this sum becomes progressively less than unity the shorter the wavelength. There is no way of telling whether or not reaction 2 has a quantum yield sufficient to account for the difference, but probably not.

(d) Other Products. The formation of polymer on the windows was noted. The quantum yield was

---

[10] (a) L. Kaplan, K. E. Wilzbach, W. G. Brown, and S. S. Yang, *J. Am. Chem. Soc.*, **87**, 675 (1965); (b) I. E. Den Besten, L. Kaplan, and K. E. Wilzbach, *ibid.*, **90**, 5868 (1968).

greater at short wavelengths than at long but in any case was low.

Many products have been reported previously upon exposure of the xylenes to radiation in this region.[11,12] These products include toluene, ethylbenzene, *o*-methylethylbenzene (from *o*-xylene), methane, and ethane. The character of the walls apparently affects the rates of formation of some of these products as does the intensity.

During the determination of the quantum yields of isomerization gas chromatography was used to search for products. No products of low molecular weight were found. Quantum yields of formation of toluene and of methylethylbenzene from *o*-xylene were well below 0.001 at 25° at all wavelengths from 2400 to 2710 Å, and in most instances no evidence could be found for their formation. Thus, under the conditions of these experiments with quite monochromatic light and low intensities, the yields of all of these substances are negligible compared to the yields of isomerization.

(e) Quenching of Excited Singlet States by 1,3-Pentadiene. Piperylene (1,3-pentadiene) has been suggested as a means of destroying triplet states of many molecules without simultaneously destroying the singlet states.[13] Its singlet state lies at too high a level to be affected by simple energy transfer from the vibrationless excited singlet states of benzene, toluene, and the xylenes. In the range 2700–2740 Å, 1,3-pentadiene shows no observable absorption. At shorter wavelengths it absorbs, and calculations should be based only on the fraction of the light absorbed by the xylene. This may not be done with accuracy since Beer's law is not rigorously obeyed.[14] Such results will be presented only qualitatively.

It seems best to present the pentadiene results in terms of a simple mechanism

$$X + h\nu = {}^1X \qquad (9)$$

$${}^1X = X + h\nu \qquad (10)$$

$${}^1X + PD = X + PD \qquad (11)$$

$${}^1X = ? \qquad (12)$$

$$Q^{-1} = 1 + \frac{k_{12}}{k_{10}} + \frac{k_{11}(PD)}{k_{10}} \qquad (13)$$

where X is a molecule of xylene and PD is a molecule of pentadiene. Step 12 is necessary because Q is not unity when (PD) = 0. From a slope of Q^{-1} *vs.* (PD) one can calculate k_{11}/k_{10}, and if k_{10} is known one may calculate an effective cross section for quenching. The values of k_{10} used[15] are as follows: (a) *o*-xylene, 6.54 $\times$ 10^6 sec^{-1}; (b) *m*-xylene, 5.99 $\times$ 10^6 sec^{-1}; (c) *p*-xylene, 1.08 $\times$ 10^7 sec^{-1}. These are based on calculated radiative lifetimes. From the intercept one can calculate k_{12}.

It is realized that this simplified treatment is semiempirical, but the trends in the results are indicated. The data are shown in Table IV.

Table IV. Quenching of the Fluorescence of Xylenes by 1,3-Pentadiene (25°)

Wavelength	Xylene	Pentadiene	k_{11}/k_{10}, ml molecule^{-1}	k_{12}/k_{10}	Effective cross section, cm^2 $\times$ 10^{16}
			o-Xylene $\times$ 10^{18}		
2710	4.6	29	4.2	1.4	2.2
	4.6	3.3	10.0	1.8	5.2
2480	4.7	16	3.4	6.9	1.8
	4.7	3.3	3.4	6.9	1.8
			m-Xylene		
2710	3.3	4.7	3.9	1.7	1.9
	3.3	17.4	6.2	1.9	3.0
	3.3	17.4	4.6	1.6	2.3
			p-Xylene		
2530	3.3	14.2	0.043	1.8	3.8
2710	4.6	29.1	0.034	1.0	3.0
2710	2.0	29.3	0.031	1.1	2.7
2710	1.99	18.2	0.029	1.1	2.6

It should be noted that the calculations of effective cross sections in Table IV depend on relatively small differences between large numbers and are subject to considerable error. The effective cross sections indicate that the collisional efficiency is fairly high at 2710 Å. Values at short wavelength scatter badly and apparently are small.

At 2710 Å inert gases (butane, *cis*-butene-2, cyclohexane) cause an apparent quenching which will be discussed later. To ascertain whether or not this apparent quenching is of the same order of magnitude, effective cross sections for this effect have been calculated. For the three xylenes, they are about 0.08 $\times$ 10^{-16} cm^2 or roughly 3 or 4% of the values for the 1,3-pentadiene. This gives some supporting evidence to the belief that 1,3-pentadiene gives a true quenching rather than merely vibrational relaxation to excited singlet-state xylene molecules.

Discussion

A detailed theoretical treatment of these data would not be warranted, but a semiempirical mechanism can be proposed

$$X + h\nu = {}^1X_v \qquad (14)$$

$${}^1X_V = X + h\nu_V \qquad (15)$$

$$= I \qquad (16)$$

$$= {}^1X_0{}^* \qquad (17)$$

$${}^1X_V + N = {}^1X_0 + N \qquad (18)$$

$${}^1X_0{}^* + N = {}^1X_0 + N \qquad (19)$$

$${}^1X_0 = X + h\nu_0 \qquad (20)$$

$$= T \qquad (21)$$

where ^1X_V is an upper-state singlet molecule in vibrational level v; I is some reaction product, perhaps an isomer; $^1X_0{}^*$ retains the vibrational energy of ^1X_V but is so widely distributed among the vibrational degrees of freedom that the reverse of (17) may be neglected. $^1X_0$ is an upper state singlet molecule with vibrational energy equilibrated with the surroundings. N is an inert foreign gas molecule. T is possibly a triplet-state molecule.

---

(11) K. E. Wilzbach and L. Kaplan, *J. Am. Chem. Soc.*, **86**, 2307 (1964).

(12) H. R. Ward, *ibid.*, **89**, 2367 (1967).

(13) A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965).

(14) H. Ishikawa and W. A. Noyes, Jr., *J. Am. Chem. Soc.*, **84**, 1502 (1962).

(15) *Cf.* I. B. Berlman, "Handbook of Fluorescence Spectra of Organic Molecules," Academic Press, New York, N. Y., 1965.

Step 15 may be neglected at wavelengths below 2590 Å and at pressures of 1 Torr or greater since no evidence is found for resonance fluorescence from either toluene[4] or the xylenes. At 2700–40 Å and perhaps at 2590 Å collisional processes cause some apparent quenching which necessitates a step such as (15).

If (15) is neglected and (N) = 0

$$Q = \frac{k_{20}}{k_{20} + k_{21}} \frac{k_{17}}{k_{16} + k_{17}} \tag{22}$$

$$\Phi_I = \frac{k_{16}}{k_{16} + k_{17}} \tag{23}$$

$$\Phi_T = \frac{k_{21}}{k_{20} + k_{21}} \frac{k_{17}}{k_{16} + k_{17}} \tag{24}$$

If (N) = ∞

$$Q = \frac{k_{20}}{k_{20} + k_{21}} \tag{25}$$

$$\Phi_I = 0 \tag{26}$$

$$\Phi_T = \frac{k_{21}}{k_{20} + k_{21}} \tag{27}$$

and

$$Q + \Phi_T = 1 \tag{28}$$

For all three xylenes the equations for Q, Φ_I, and Φ_T show trends in agreement with the data at wavelengths of 2590 Å and below. As one would expect constants change with wavelength. The ratio k_{16}/k_{17} is 20–50 at 2400 Å and decreases to 1–3 at 2530 Å. Effective cross sections for (18) vary from about 0.1×10^{-16} cm^2 at 2400 Å to about 2 or 3×10^{-16} cm^2 at 2530 Å. Thus, internal rearrangement of vibrational energy may not be neglected under the conditions of these experiments.

A detailed statistical treatment based on a large array of vibrational levels would not be justified at the present time. Since actual rate constants derived from this mechanism would have little quantitative significance, they will not be reproduced in detail.

For any given xylene there will be six ways of forming dimethylbenzvalene with the following new bonds: (a) 1–3 and 2–4; (b) 2–4 and 3–5; (c) 3–5 and 4–6; (d) 4–6 and 5–1; (e) 5–1 and 6–2; (f) 6–2 and 1–3. For *o*-xylene, four of these could not lead to *m*-xylene, and of the remaining two, each would have about an equal chance of returning to *o*-xylene. Thus, in the ideal case the maximum yield of *m*-xylene would be 0.17, or conversely Φ_I would be about six times the value of Φ_{X^m}. These geometrical considerations coupled with the other factors already discussed might mean that Φ_I could be much greater than 0.5.

The case for *m*-xylene is more interesting since of the six dimethylbenzvalenes, two forms can give *ortho* and two can give *para*. Thus, the yield of each might be 0.17 and the total yield 0.33. This means that Φ_I could be as much as three times the sum of Φ_{X^o} and Φ_{X^p}.

For *p*-xylene, four of the dimethylbenzvalenes can give *m*-xylene each with perhaps a probability of 0.5 so that Φ_I might be three times Φ_{X^m}. When all of these factors are considered, it is seen that the yield of intermediate isomer I may provide most of the deficiency in energy balance. Much further work along these lines is necessary.

The situation at 2710–2740 Å is of special interest. These measurements were made at the peaks of absorption in this region. There is no reason to believe that different electronic states are involved and presumably absorption arises from a vibrational level of the ground state greater than the zeroth level. Perhaps 5–10% of the molecules would be found in these levels at room temperature. Absorption probably would lead to formation of excited singlet state molecules with less than the mean vibrational energy. Thus, vibrational relaxation might lead to "warming" rather than "cooling" the excited molecules.

Quite evidently the mechanism embodied in reactions 14–21 does not fit this case, particularly since the asymptotes seem to be lower than at shorter wavelengths. They are as follows: *o*-xylene, (0.34) (<2590), 0.30 (2710); *m*-xylene, (0.30) (<2590), 0.27 (2725); *p*-xylene, (0.50) (<2590), 0.44 (2740).

It should be noted that the xylenes at these long wavelengths follow the same trend as observed for benzene by Kistiakowsky and Parmenter[16] and by Anderson and Kistiakowsky[17] at 2537 Å.

A step which would give the correct trend to the results would be

$${}^1X_V + N = {}^3(T) \tag{29}$$

This step would lead to the following expression for Q when the pressure is large and provided (15) is neglected

$$Q = \frac{k_{20}}{k_{20} + k_{21}} \frac{k_{18}}{k_{18} + k_{19}} \tag{30}$$

which could be lower than $k_{20}/(k_{20} + k_{21})$ observed at short wavelengths.

This suggestion is put forward merely to indicate that perturbations by collisions at very low vibrational levels might enhance triplet state formation. Little more can be said at the present time.

Acknowledgment. The authors wish to thank Drs. K. E. Wilzbach and L. Kaplan of the Argonne National Laboratory, Dr. Duncan Anderson of the University of Texas, and Mr. J. C. André of the University of Nancy, France, for many helpful discussions.

---

[16] G. B. Kistiakowsky and C. S. Parmenter, *J. Chem. Phys.*, **42**, 2942 (1965).

[17] E. Anderson and G. B. Kistiakowsky, *ibid.*, **48**, 4787 (1968).