

The present results for  $\text{BH}_3$  to  $\text{BF}_3$  and the results of Ha and Allen<sup>27</sup> for  $\text{CH}_4$  to  $\text{CHF}_3$  show the changes of both B and C 1s levels in the changing environment of successive fluorination. The orbital energies and atomic charges calculated on the basis of the population analyses are plotted in Figure 6. There is indeed a good linear correlation of binding energy *vs.* this definition of charge. Note that in both series the 1s binding energies of the multiply fluorinated molecules are shifted from the nonfluorinated molecule by amounts almost precisely a multiple of the shift for a single fluorination. It is interesting that the binding energy of B 1s should correlate linearly with overall B charge, since we have seen that the partitioning of atomic populations into  $\sigma$  and  $\pi$  contributions changes through

(32) M. E. Schwartz, C. A. Coulson, and L. C. Allen, *J. Amer. Chem. Soc.*, in press.

the series. However, the N and S experimental results are for a very wide variety of molecules, and the overall energy *vs.* charge correlation seems still to hold reasonably well, even though the charges are difficult to define unambiguously.<sup>32</sup>

There are no experimental results for direct comparison with these calculated ones. We look forward to the experimental measurements on the systems we have studied.<sup>33</sup>

(33) NOTE ADDED IN PROOF. Recent experimental studies<sup>34</sup> of the halomethanes and recent theoretical studies<sup>35</sup> of C 1s in several molecules have both shown that 1s energy shifts may be overestimated by MO wave functions expanded in terms of these accurate atomic functions. More flexibility as a molecular basis is required for satisfactory calculations of inner-shell shifts. M. E. S. will report on such studies relevant to the boron compounds later. The trends of linearity and additivity do seem to be valid, however.<sup>32, 34, 35</sup>

(34) T. D. Thomas, *J. Amer. Chem. Soc.*, in press.

(35) M. E. Schwartz, submitted for publication.

## Kinetics of the Cycloaddition of Photoexcited Benzene to 2-Butene in the Gas Phase<sup>1a</sup>

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**Abstract:** Cycloaddition of the photoexcited benzene to *cis*- and *trans*-2-butene in the gas phase has been studied at 25°. Different adducts are formed from the two geometric isomers of 2-butene. Nmr analyses of the addition products show that the two main adducts from *trans*-2-butene are two stereoisomers (*endo,exo* and *exo,endo*) of the major adduct from *cis*-2-butene (6,7-dimethyltricyclo[3.3.0.0<sup>2,5</sup>]oct-3-ene). The cycloadditions to both *cis*- and *trans*-2-butene take place with retention of configuration of the butene moiety. This, together with the effects of small additions of oxygen and biacetyl, indicates that the excited singlet of benzene, and not the triplet <sup>3</sup>B<sub>1u</sub>, is involved in the photoaddition. The kinetics of the photoaddition has been studied and is discussed.

Photoaddition of benzene to *cis*-2-butene in the uv spectral region at 2370–2530 Å has been observed both in the gas phase<sup>2a</sup> and in the liquid phase.<sup>2b</sup> These and other photoaddition and photoisomerization reactions of the benzene ring have been recently reviewed by Bryce-Smith.<sup>3a</sup> An excited form of benzene, a singlet biradical, has been suggested by Bryce-Smith and Longuet-Higgins<sup>3b</sup> as the common precursor for benzene addition to olefins and for its isomerization to benzvalene and fulvene. However, some questions have been raised in connection with this postulate. Kaplan and Wilzbach<sup>2a</sup> have found that the yields of benzvalene and of the adduct to *cis*-2-butene have opposite dependences on the wavelength of the exciting radiation and concluded that, if there is a common intermediate, the ratio of products must vary with its energy content.

The present work is an extension of our recent study<sup>4</sup> of the quenching of benzene fluorescence by hydrocar-

bons at relatively high pressures, in which it has been found that monoolefins of molecular weight greater than 2-butene show very small but measurable quenching efficiencies. This result suggests the possibility that the fluorescence quenching and adduct formation are related processes, both involving the excited singlet benzene, <sup>1</sup>B<sub>2u</sub>. We have, therefore, investigated the kinetics and the stereochemistry of adduct formation between benzene and *cis*- and *trans*-2-butene in order to obtain further information about the photoaddition process.

### Experimental Section

A U-shaped quartz tube, 8-mm i.d., 65 mm high, and with the two arms 30 mm apart, was used as the reactor. Its total volume was 8 ml. The lower half of the reactor was irradiated by a Hanovia 673A 10 medium-pressure mercury arc through two filters, a Corning 9-54 glass filter and a 50-mm long quartz cell containing mercury vapor and 50 Torr hydrogen.

2-Butene isomers were analyzed on a propylene carbonate on fire brick column at 0°. The products of photoaddition were analyzed on a 20% silicone rubber, SE-30, on Anakrom AW (Analytical Engineering Laboratories) column, at 125°. Helium carrier gas and thermal conductivity detectors were used. Mass spectrometer (Atlas CH-4)-gas chromatography combination and nmr spectroscopy (Varian Associates HA-100D) were used to determine the mass and the structure of the products.

(1) (a) Issued as NRC No. 11245; (b) National Research Council postdoctoral fellow.

(2) (a) L. Kaplan and K. E. Wilzbach, *J. Amer. Chem. Soc.*, **90**, 3291 (1968); (b) K. E. Wilzbach and L. Kaplan, *ibid.*, **88**, 2066 (1966).

(3) (a) D. Bryce-Smith, *Pure Appl. Chem.*, **16**, 47 (1968); (b) D. Bryce-Smith and H. C. Longuet-Higgins, *Chem. Commun.*, 593 (1966).

(4) A. Morikawa and R. J. Cvetanovic, *J. Chem. Phys.*, **49**, 1214 (1968).

**Table I.** Chemical Shifts<sup>a</sup> for the Protons of the Three Stereoisomers of 6,7-Dimethyltricyclo[3.3.0.0<sup>2,8</sup>]oct-3-ene (I)

Stereoisomer	Methyl protons		Methine protons		Protons derived from benzene					
	6	7	6	7	1	2	3	4	5	8
Compound 8 I ( <i>endo,endo</i> ) <sup>b</sup>	0.98	0.78	2.45	2.65	2.55 <sup>c</sup>	1.62 <sup>c</sup>	5.58 <sup>c</sup>	5.48 <sup>c</sup>	2.83 <sup>c</sup>	1.75 <sup>c</sup>
Compound 4 I ( <i>endo,exo</i> )	0.985	1.11	1.68	2.04	2.66	1.62	5.55	5.30	2.69	1.67
Compound 5 I ( <i>exo,endo</i> )	0.73	1.09	1.90	1.30	2.40	1.70	5.57	5.41	2.86	1.92

<sup>a</sup> The proton resonance spectra were obtained on a Varian Associates HA-100D spectrometer at room temperature. Chemical shifts are in ppm to low field of tetramethylsilane. The numbers (1-8) in the table heading indicate the carbon atom positions in 6,7-dimethyltricyclo[3.3.0.0<sup>2,8</sup>]oct-3-ene. <sup>b</sup> Stereochemical assignments as given in ref 2b. It is possible that the *endo,endo* assignments for the two methyl groups in compound 8 should be reversed, as discussed in the text, in which case the assignments for the compounds 4 and 5 should be reversed also (*endo* should read *exo* and *exo* should read *endo* throughout). <sup>c</sup> Identical with the values in ref 2b.

Phillips Research Grade propane, *n*-butane, isobutane, *cis*- and *trans*-2-butene, and *n*-pentane were used after several bulb-to-bulb distillations *in vacuo*. Matheson Co. N<sub>2</sub>O, Xe, CO<sub>2</sub>, and SF<sub>6</sub> were frozen into a liquid nitrogen trap and the middle fraction of the distillate was stored for use. Benzene (Baker and Adamson ACS reagent grade) was purified by several recrystallizations, dried on silica gel, and distilled *in vacuo*. The middle fraction was transferred to the storage bulb and thoroughly degassed.

## Results and Discussion

### Formation of the Photoadducts of Benzene to 2-Butene.

Gas chromatographic analysis on the silicone rubber column of the products from a mixture of benzene (49 Torr) with equal amounts of *cis*- and *trans*-2-butene (393 Torr each) after 2 hr of irradiation shows at least ten product peaks (top tracing in Figure 1). Irradiated

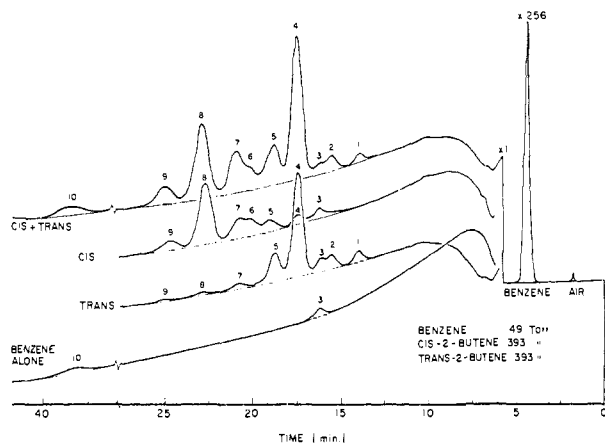


Figure 1. Chromatograms of the products from irradiated benzene alone (49 Torr) and its mixtures with *trans*-2-butene (393 Torr), *cis*-2-butene (393 Torr), and 1:1 *cis*-2-butene (393 Torr) + *trans*-2-butene (393 Torr) (irradiation 2 hr at 25°).

benzene alone (49 Torr) shows the presence of peaks 3 and 10 only (bottom tracing). With the exception of these two peaks, the remaining eight peaks have been shown by direct mass spectrometric analysis of the gas chromatographic eluates to have a total molecular weight of 134, *i.e.*, the sum of the molecular weights of benzene and butene. These eight compounds appear therefore to be adducts of benzene to 2-butene. Compound 10 has a molecular weight of about 390, which is close to the upper limit of the resolution of the instrument and is therefore somewhat uncertain. No attempt has been made to determine the molecular weight of compound 3.

The chromatograms of the products from a benzene-*cis*-2-butene mixture and a benzene-*trans*-2-butene mixture, labeled in Figure 1 *cis* and *trans*, respectively, indicate that four compounds, 6, 7, 8, and 9, are adducts of benzene to *cis*-2-butene and four, 1, 2, 4, and 5, are adducts of benzene to *trans*-2-butene. The formation of different adducts from *cis*- and *trans*-2-butene shows retention of geometric configuration of the 2-butene in the photoadducts.

Irradiation of a liquid mixture of benzene and *trans*-2-butene gives chromatograms with two major peaks and several minor ones. The two major products have again molecular weights of 134 and, when mixed with the analogous gas-phase product mixture, their gas chromatographic peaks coincide with those of compounds 4 and 5, the latter having half the peak area of the former. Irradiation of a liquid mixture of benzene and *cis*-2-butene gives chromatograms with only one major peak and this was found to coincide with peak 8. The identity of the major products formed in the liquid with those formed in the gas-phase reactions was supported by their essentially identical mass spectra, although there was a relatively large benzene background and some memory of the preceding peak because of incomplete separation. Moreover, the mass spectra of the three major adducts, compounds 4, 5, and 8, were mutually very similar, suggesting closely similar molecular structures.

**The Molecular Structures of the Major Adducts (Compounds 4, 5, and 8).** Samples for the nmr analysis were prepared from the liquid phase reaction products and were purified by preparative gas chromatography using again the 20% silicone rubber, SE-30, on Anakrom AW column at 125°. Samples of the same adducts with benzene-*d*<sub>6</sub> were obtained similarly. All the samples were dissolved in carbon tetrachloride containing tetramethylsilane (TMS) as internal standard.

Wilzbach and Kaplan<sup>2b</sup> have identified by nmr analysis the product of photoaddition of benzene to *cis*-2-butene, which is identical with compound 8 in the present work, as 6,7-dimethyltricyclo[3.3.0.0<sup>2,8</sup>]oct-3-ene (I). The chemical shifts obtained by them for the protons derived from the benzene moiety are listed in the first row of Table I (protons 1, 2, 3, 4, 5, and 8). Those for the protons arising from *cis*-2-butene were measured more accurately in the present study by forming the adduct (compound 8) with deuteriobenzene and by spin decoupling. The almost complete removal of spin coupling to the benzene hydrogens greatly simplified the spectra. The chemical shifts for the methyl

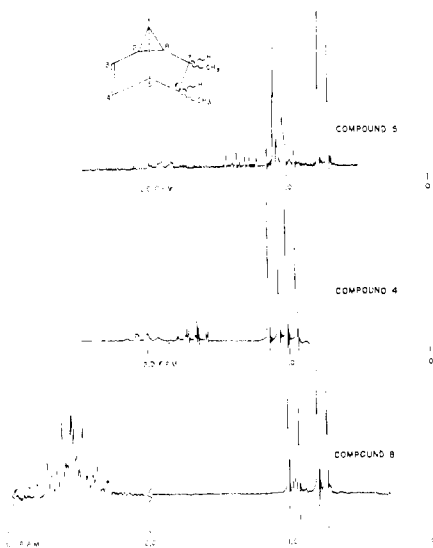


Figure 2. Nmr spectra of compounds 8, 4, and 5 obtained from  $2\text{-C}_4\text{H}_8$  and  $\text{C}_6\text{D}_6$ . The signals from the methyl and methine protons are shown ( $\text{CCl}_4$  solutions with TMS as internal standard).

and methine protons thus obtained are shown in the first row of Table I (for carbon atoms 6 and 7). Similar spectra for the principal (compound 4) and the less abundant (compound 5) adducts with *trans*-2-butene are shown in Figure 2. The chemical shifts are listed in the second and third row of Table I.

Wilzbach and Kaplan<sup>2b</sup> have suggested that the strong coupling between protons 5 and 6 and between protons 8 and 7 probably indicates that the methyl groups in compound 8 are both in the *endo* position. In Figure 2 it can be seen that the 7 proton in compound 4 and the 6 proton in compound 5 have considerably broadened signals compared with the other methine protons. This is attributed to spin coupling with adjacent deuterium atoms. Since proton-deuterium coupling is much smaller than the analogous proton-proton coupling, this strongly suggests that the protons giving the broadened signals are most strongly spin-coupled to an adjacent hydrogen atom. The magnitudes of spin-spin coupling constants are quite stereospecific and therefore the larger coupling constants observed for these two protons suggest that they have a different stereochemistry from those in compound 8. This also suggests the possibility that the methyl groups in compound 8 are actually both in the *exo* rather than in the *endo* position. In Table I, however, the original assignment<sup>2b</sup> of the configuration of compound 8 is used and the stereochemistry of the compounds 4 and 5 is given relative to it. If the *endo,endo* assignment for compound 8 is in error and should be changed to *exo,exo*, then the *exo,endo* assignments in compounds 4 and 5 should also be reversed.

All the assignments were confirmed by multiple spin-decoupling studies. For example, the methyl and methine resonances on the same carbon atoms (6 or 7) can be determined by irradiating one of the methine protons and noting which methyl spin-coupled doublet is collapsed. This was done for all the compounds prepared with deuterated benzene. The spectrum of compound 4 prepared from normal benzene is shown in Figure 3. When it is irradiated at 2.69 ppm from TMS, the signals at 5.30 and 1.68 are altered. The signal at

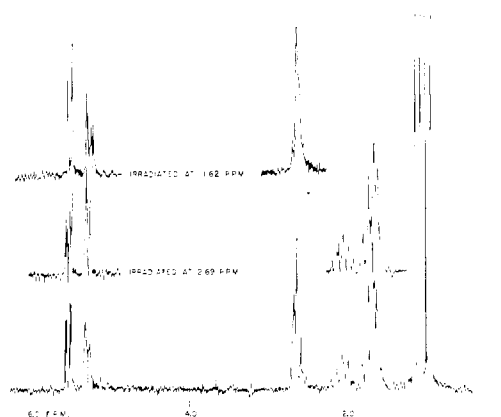


Figure 3. The nmr spectrum of compound 4, obtained from *trans*- $\text{C}_4\text{H}_8$  and  $\text{C}_6\text{H}_6$ , and the decoupling experiments ( $\text{CCl}_4$  solution with TMS as internal standard).

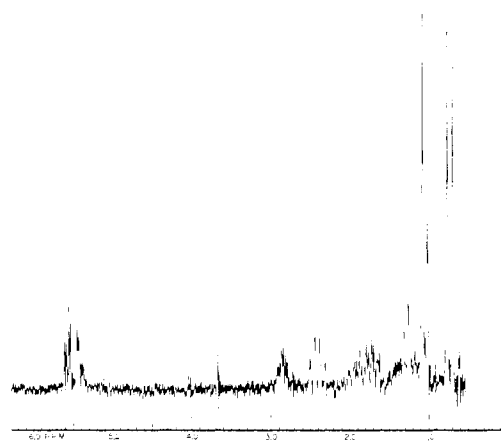


Figure 4. The nmr spectrum of compound 5, obtained from *trans*- $\text{C}_4\text{H}_8$  and  $\text{C}_6\text{H}_6$  ( $\text{CCl}_4$  solution with TMS as internal standard).

1.68 must be from proton 6 or 7. However, the only way both an olefinic proton and a methine proton can be simultaneously affected is if they are protons 4 and 6, while proton 5 is being irradiated. Therefore, protons 4, 5, and 6 can have their chemical shifts positively assigned, and, by elimination, protons 3 and 7 are also assigned. The pattern at 5.55 ppm is collapsed by irradiating at 1.62 ppm and this also collapses the peak at 2.66 ppm. This therefore assigns the positions of protons 2 and 3, leaving protons 1 and 8, one of which must be at 2.66 ppm. Since it was also found that irradiating at 1.67 ppm affected the signal of proton 7, proton 8 is at 1.67 ppm, and therefore proton 1 must be the one at 2.66 ppm. This completes the assignment for compound 4. A similar treatment was used to assign the peaks for compound 5, whose proton resonance spectrum is shown in Figure 4.

The nmr analysis shows, therefore, that compounds 4 and 5 are two stereoisomers of compound 8, with one of the two methyl substituents on carbons 6 and 7 changed from the *endo* to the *exo* configuration (or *vice versa*). Thus in the major photoadducts of benzene to 2-butene the geometric configuration of the olefin is preserved. *cis*-2-Butene forms one major adduct with the two methyl groups *cis* to each other, as has been suggested earlier by Wilzbach and Kaplan;<sup>2b</sup> *trans*-2-butene forms the two possible stereoisomers with the methyl groups *trans* to each other. These three com-

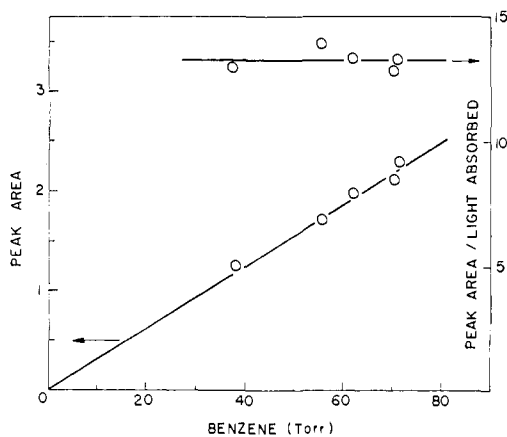


Figure 5. The yields of compound **8** as a function of benzene pressure (*cis*-2-butene, 421 Torr, irradiation 2 hr at 25°).

pounds are three of the possible four stereoisomers of 6,7-dimethyltricyclo[3.3.0.0.2<sup>8</sup>]oct-3-ene. They are almost the exclusive photoadducts in the liquid phase. In the gas phase smaller amounts of several other photoadducts are formed as well but they have not been identified yet.

**Rates of Formation of the Photoadducts in the Gas Phase.** Mixtures of 60 Torr benzene, 274 Torr *cis*-2-butene, and 411 Torr SF<sub>6</sub> were irradiated for various time intervals between 0.5 and 6 hr. The volatile product distilled out at -78° was *trans*-2-butene, as determined on the propylene carbonate column at 0°. Since the benzene-photosensitized isomerization of *cis*-2-butene at relatively high pressure is zero order in *cis*-2-butene pressure and the fraction of *trans*-2-butene formed ( $x$ ) at equilibrium is close to 0.5,<sup>5-7</sup> a plot of  $\log [0.5 - x]$  vs. time should be linear. Linear plots were obtained up to 3-hr irradiation, after which  $x$  tended to be smaller than expected from the extrapolations of the linear plots.

Gas chromatograms of the product nonvolatile at -78° were obtained on the silicone rubber column at 125°; an example has already been shown in Figure 1. The planimetric peak areas of compound **8** were proportional to the irradiation time up to 3 hr and then tended to be smaller than expected from the proportionality. The decline in the rates of adduct formation,  $R_A$ , and of *cis*-2-butene isomerization,  $R_T$ , was probably due to decreased transparency of the reactor, since after long irradiation small amounts of polymer deposit became noticeable. In view of this, in all subsequent kinetic experiments reactants were irradiated for 2 hr.

**Dependence of  $R_A$  on Benzene Pressure.** Figure 5 shows a plot of the peak areas of compound **8** at different benzene pressures and at a constant pressure of 421 Torr *cis*-2-butene. The corresponding values in arbitrary units of the peak areas divided by  $I_a$ , the amount of light absorbed, are also shown. The latter have been determined from the rates of *trans*-2-butene formation,  $R_T$ . The following somewhat simplified reaction scheme is applicable under conditions used.

(5) M. Tanaka, T. Terao, and S. Sato, *Bull. Chem. Soc. Jap.*, **38**, 1645 (1963).

(6) G. A. Haninger, Jr., and E. K. C. Lee, *J. Phys. Chem.*, **71**, 3104 (1967).

(7) A. Morikawa and R. J. Cvetanović, *Can. J. Chem.*, **46**, 1813 (1968).

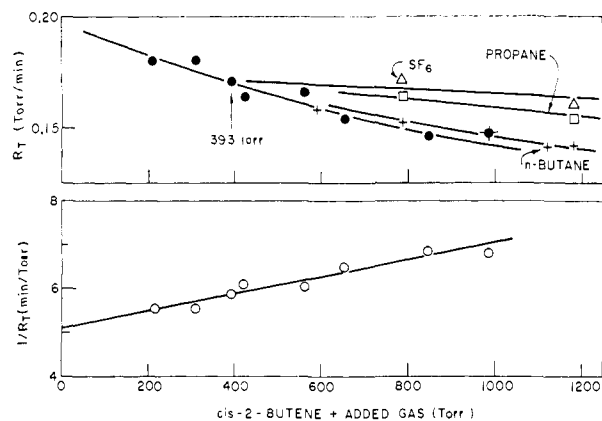
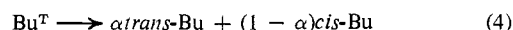
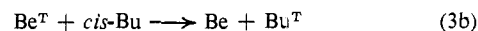
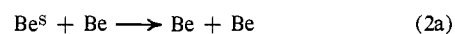


Figure 6. Rates of formation of *trans*-2-butene ( $R_T$ ) as a function of *cis*-2-butene pressure and the effect of added gases (benzene 49 Torr initially, irradiation 2 hr at 25°).



The notation is similar to that in the previous papers.<sup>4,7</sup> Adduct formation is much slower than the isomerization and is neglected. At the high pressures of *cis*-2-butene, the phosphorescence and radiationless transition of the benzene triplet ( $\text{Be}^T$ ) are also neglected. As already mentioned,  $\alpha \approx 0.5$ . The steady state treatment gives

$$R_T = \alpha I_a k_{1b} / (k_1 + k_{2a}[\text{Be}] + k_{2b}[\text{cis-Bu}]) \quad (5)$$

Since the rate constants  $k_1$ ,  $k_{2a}$ , and  $k_{2b}$  are known, and  $k_{1b}/k_1 = 0.63$ ,<sup>8</sup>  $I_a$  can be evaluated from eq 5 and has been used to plot the peak area/ $I_a$  ratios in Figure 5. It is clear that the peak areas of compound **8** are proportional to benzene pressure, but  $I_a$  shows a similar dependence and the quantum yields of compound **8**, i.e., the  $R_A/I_a$  ratios, remain independent of benzene pressure.

Figure 6 shows the decline in  $R_T$  (filled circles) with increasing *cis*-2-butene at a constant pressure of 49 Torr benzene. Under such conditions, according to eq 5, a plot of  $1/R_T$  vs.  $[\text{cis-Bu}]$  should be linear. Within an appreciable experimental scatter, a linear plot is obtained (open circles). The slope to intercept ratio equals  $k_{2b}/(k_1 + k_{2a}[\text{Be}])$  and, with<sup>9,10</sup>  $(k_1 + k_{2a}[\text{Be}]) = 1.3 \times 10^7 \text{ sec}^{-1}$ , it gives the rate constant of the quenching of  $\text{Be}^S$  by *cis*-2-butene,  $k_{2b} = 1.5 \times 10^{13} \text{ cc/molecule sec}$ . This kinetic value of  $k_{2b}$  is in adequate agreement with the corresponding "intrinsic" rate constant  $k_{2b}'$  ( $1.2 \times 10^{13} \text{ cc/molecule sec}$ ) estimated approximately from the quenching of benzene fluorescence by *cis*-2-butene.<sup>4,9</sup> Figure 6 also shows that additions of up to 800 Torr

(8) R. B. Cundall and A. S. Davies, *Trans. Faraday Soc.*, **62**, 1151 (1966).

(9) The quoted values of the rate constants from earlier publications have been revised in agreement with the new literature values of the lifetimes of  $\text{Be}^S$  and  $\text{Be}^T$ , as explained in ref 10.

(10) A. Morikawa and R. J. Cvetanović, *J. Chem. Phys.*, in press.

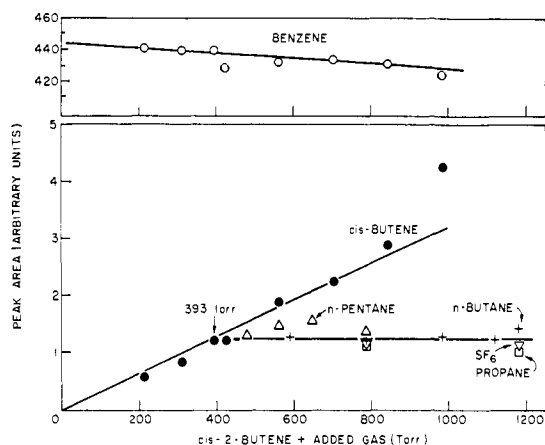


Figure 7. Rates of formation of compound 8 as a function of *cis*-2-butene pressure and the effect of added gases (benzene 49 Torr initially, irradiation 2 hr at 25°).

SF<sub>6</sub> or propane to 49 Torr benzene and 393 Torr *cis*-2-butene cause at best only a very minor decline in  $R_T$ . At these pressures of benzene and *cis*-2-butene, Be<sup>S</sup> is apparently already almost completely vibrationally deactivated and further additions of inert gas have relatively little effect on its conversion of Be<sup>T</sup> and thus on  $R_T$ .<sup>11</sup> The value of  $k_{2b}$  should therefore be close to the intrinsic quenching rate ( $k_{2b}'$ ) of Be<sup>S</sup> by *cis*-2-butene.<sup>4,9</sup>

Unlike propane and SF<sub>6</sub>, *n*-butane has about the same effect on  $R_T$  as *cis*-2-butene. This apparent anomaly will be discussed below.

**Dependence of  $R_A$  on the 2-Butene Pressure.** Figure 7 shows the linear increase of the yield of compound 8 (filled circles) with increasing *cis*-2-butene pressure (up to 800 Torr) at a constant pressure of 49 Torr benzene. The upper part of Figure 7 shows the simultaneous decline in the peak areas of benzene (open circles). Assuming that the ratio of the detector responses of compound 8 and benzene is the same as that of butylbenzene and benzene (1.6), the data in Figure 7 show that about 12% of the benzene consumed is recovered as compound 8. Polymer formation is perhaps responsible for the larger part of benzene consumption.

The linear increase in  $R_A$  with *cis*-2-butene is not a pressure effect involving collisional deactivation of "hot" (excited to very high vibrational levels) precursors, intermediates, or adducts. This is shown by the lack of an effect of additions to 393 Torr *cis*-2-butene of up to 800 Torr SF<sub>6</sub>, propane, or *n*-butane. There is, however, a slight pressure effect of *n*-pentane. The accelerating effect of *n*-pentane is considerably more pronounced on the yield of compound 7 (Figure 8), where *n*-butane also shows some accelerating efficiency although much weaker than *n*-pentane. The earlier mentioned effect of *n*-butane on  $R_T$  is probably a related phenomenon. These effects are not fully understood and can be discussed only in a tentative manner. Hydrogen atom abstraction from these paraffins is apparently not involved. In experiments with *n*-C<sub>4</sub>D<sub>10</sub> added to 2-C<sub>4</sub>H<sub>8</sub> (1:1 *cis* and *trans*)-C<sub>6</sub>H<sub>6</sub> mixtures, no deuterium enrichment was observed in any of the adducts (compounds 4, 5, 6, 7, 8, and 9 were checked). The accelerating effects may perhaps be explained by a

(11) S. J. Strickler and R. J. Watts, *J. Chem. Phys.*, **44**, 426 (1966).

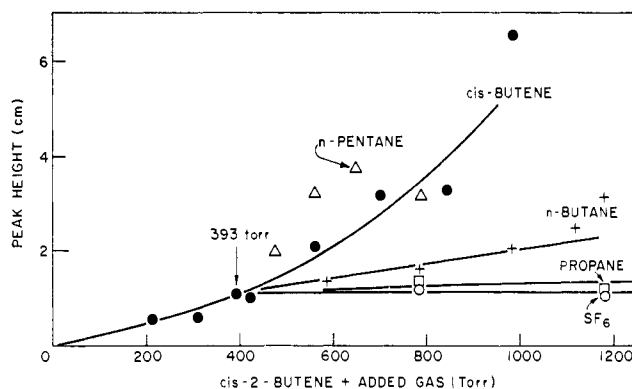


Figure 8. Rates of formation of compound 7 as a function of *cis*-2-butene pressure and the effect of added gases (benzene 49 Torr initially, irradiation 2 hr at 25°).

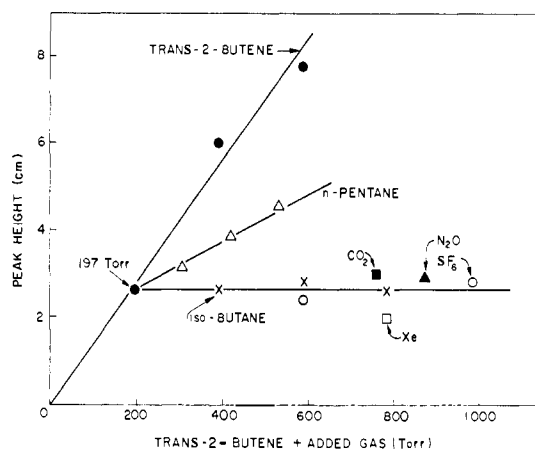


Figure 9. Rates of formation of compound 4 as a function of the pressure of *trans*-2-butene and the effect of added gases (benzene 49 Torr initially, irradiation 2 hr at 25°).

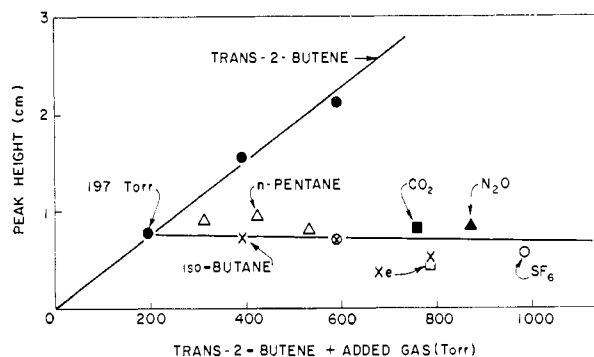


Figure 10. Rates of formation of compound 5 as a function of the pressure of *trans*-2-butene and the effect of added gases (benzene 49 Torr initially, irradiation 2 hr at 25°).

specific ability of some paraffins to activate or deactivate the *low lying* vibrations of the excited benzene intermediates. Such vibrations may have an important effect on the rates of their reactions (internal conversion, intersystem crossing, isomerization, etc.). However, considerable further work will be required before a detailed explanation can be formulated.

The dependence of the rates of formation of the adducts 4 and 5 on pressure are shown in Figures 9 and 10. Mixtures of 49 Torr benzene and various pressures of *trans*-2-butene were used. The rates increase lin-

early with *trans*-2-butene. Additions of a number of foreign gases (isobutane, SF<sub>6</sub>, Xe, CO<sub>2</sub>, N<sub>2</sub>O) to 197 Torr *trans*-2-butene and 49 Torr benzene have little effect. *n*-Pentane is again an exception since it shows an accelerating effect.

It is evident that the kinetic behavior of the adducts **4**, **5**, and **8** is the same. The rates of adduct formation are proportional to the amount of light absorbed and to the pressure of *trans*- or *cis*-2-butene, but are independent of benzene pressure (except to the extent that it affects the amount of light absorbed). These results strongly suggest a reaction of 2-butene with an excited benzene intermediate which competitively undergoes other reactions. The additions are stereospecific, which would be expected for a cycloaddition of a singlet intermediate to 2-butene. However, stereospecificity may be preserved even with a triplet adduct if an intermediate biradical undergoes the ring closure appreciably more rapidly than the rotation around the original double bond in 2-butene. It is therefore not possible on the strength of the observed stereospecificity alone to identify unequivocally the excited state of benzene which adds to 2-butene.

**Effect of Biacetyl and Oxygen on the Rates of Adduct Formation.** The effects of small amounts of oxygen or biacetyl added to mixtures of 49 Torr benzene and 393 Torr *cis*-2-butene are shown in Table II.

**Table II.** The Effect of Additions of Small Amounts of Biacetyl and of O<sub>2</sub> on  $R_T$  and  $R_A$ <sup>a</sup>

Added gas	Pressure of added gas, Torr	<i>trans</i> -2-Butene formed, %	Peak height of adduct <b>8</b> , cm
None	0	5.7	3.6
Oxygen	1.1	5.2	3.1
	2.3	5.9	2.9
	4.6	6.0	1.8
Biacetyl	4.6	4.3	2.1

<sup>a</sup> 25°, irradiation 2 hr, benzene pressure 49 Torr, *cis*-2-butene pressure 393 Torr.

Oxygen is known<sup>12</sup> to quench strongly the excited singlet benzene but its quenching efficiency of the triplet <sup>3</sup>B<sub>1u</sub> state is almost the same as that of 2-butene.<sup>10</sup> Since the concentration of oxygen added was very much smaller than that of *cis*-2-butene, and because oxygen appears to quench the excited singlet of benzene by converting it to the <sup>3</sup>B<sub>1u</sub> state,<sup>10</sup> the species responsible for the 2-butene isomerization, its effect on  $R_T$  should be very small or negligible. The results in Table II show that  $R_T$  is indeed not affected by the oxygen added.

The ratio of the concentration of the excited singlet benzene (Be<sup>S</sup>) in the presence of an added quencher (Q), such as oxygen or biacetyl, to that in its absence is

$$\frac{[\text{Be}^{\text{S}}]_{\text{Q}}}{[\text{Be}^{\text{S}}]} = \frac{k_1 + k_{2a}[\text{Be}] + k_{2b}[\text{cis-Bu}]}{k_1 + k_{2a}[\text{Be}] + k_{2b}[\text{cis-Bu}] + k_{2b}''[\text{Q}]} \quad (6)$$

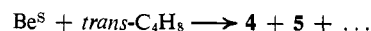
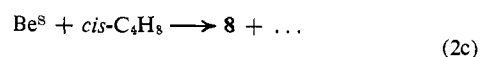
where  $k_{2b}''$  is the rate constant of the quenching of the

(12) H. Ishikawa and W. A. Noyes, Jr., *J. Chem. Phys.*, **37**, 583 (1962).

benzene singlet by Q. For oxygen<sup>9,12</sup>  $k_{2b}'' = 1.6 \times 10^{-10}$  cc/molecule sec and therefore, from eq 6 and with  $k_{2b} = 1.5 \times 10^{-13}$  cc/molecule sec,  $[\text{Be}^{\text{S}}]_{\text{O}_2}/[\text{Be}^{\text{S}}] = 0.40$  at 4.6 Torr O<sub>2</sub>. This is in fair agreement with the experimental value of 0.5 from Table II, especially considering some uncertainty in the pressure of oxygen (introduced into the reactor in which all the reactants were frozen beforehand).

Biacetyl is also an efficient quencher of the singlet benzene with<sup>9,12</sup>  $k_{2b}'' = 1.7 \times 10^{-10}$  cc/molecule sec. From eq 6  $[\text{Be}^{\text{S}}]_{\text{biacetyl}}/[\text{Be}^{\text{S}}] = 0.4$  at 4.6 Torr, in approximate agreement with the value from Table II of 0.58. In this case  $R_T$  would also be expected to decrease because biacetyl destructs the <sup>1</sup>B<sub>2u</sub> state, the precursor of <sup>3</sup>B<sub>1u</sub>. A decrease in  $R_T$  is observed although it is somewhat smaller than the decrease in the yield of the adduct.

The effects of oxygen and biacetyl additions strongly suggest that the excited singlet benzene (or a derivative from it such as the postulated<sup>3</sup> singlet biradical) and not the triplet <sup>3</sup>B<sub>1u</sub> is involved in the formation of the photoadduct. The formation of the adducts may therefore be represented by the following reactions, which should be added to reaction 2b in the earlier scheme



The rate of formation of compound **8** ( $R_{A8}$ ), for example, is then

$$R_{A8} = k_{2c8} \frac{[\text{cis-Bu}](I_a)}{k_1 + k_{2a}[\text{Be}] + k_{2b}[\text{cis-Bu}]} \quad (7)$$

Equation 7 predicts linear dependence of  $R_{A8}$  on  $[\text{cis-Bu}]$  only at small *cis*-Bu concentrations. Under the conditions of the experiments in Figure 7 the term  $k_{2b}[\text{cis-Bu}]$  in the denominator of eq 7 tends to be appreciable (about 20% of the value of the denominator at 800 Torr *cis*-2-butene) and some leveling off of  $R_A$  should become noticeable. The fact that this is not observed suggests a compensating self-accelerating effect similar to that exhibited by *n*-pentane and *n*-butane discussed above. A support for this view can be obtained from the chromatograms in Figure 1 which indicate an actual increase in the yields of the three main adducts (**4**, **5**, and **8**) in 1:1 mixtures of *cis*- and *trans*-2-butene, relative to the yields obtained with pure *cis*- and *trans*-2-butene, respectively. Since in the mixture the amount of each of the two olefins was the same as in the experiments with pure *cis*- and pure *trans*-2-butene, without an accelerating effect the yields of the adducts in the mixture should remain unaltered.

The quantum yield of the photoadducts in the gas phase is evidently dependent on the conditions. In the present experiments at 900 Torr *cis*-2-butene the quantum yield of the adduct **8** is estimated to be about  $3 \times 10^{-3}$ , which is less, by about a factor of 3, than that estimated by Kaplan and Wilzbach<sup>2a</sup> for 1 atm of *cis*-2-butene.

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