

is increased. The detailed models of the diffusion processes need further investigation. Nevertheless, for the sake of simplicity of expressions, the terms mentioned above may be used since they do not distort the real meaning of the investigated phenomena.

Acknowledgments.—In conclusion we wish to acknowledge the financial support for this study

by the National Science Foundation. Investigation of trifluoromethyl radicals was partially supported by the Office of Ordnance Research of the U. S. Army through a grant DA-30-115-ORD-678. We wish also to thank Dr. A. Stefani for his participation in the studies of trifluoromethyl radicals and for his help in preparation of the labeled acetyl peroxide.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY COLLEGE OF FORESTRY AT SYRACUSE UNIVERSITY, SYRACUSE 10, NEW YORK]

Methyl Affinities of Some Cyclic Olefins and Polyenes

BY J. GRESSER, A. RAJBENBACH AND M. SZWARC

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Methyl affinities of the following hydrocarbons were determined: cyclopentene, cyclohexene, cycloheptene, cyclooctene, norbornene, cyclopentadiene, 1,3-cyclohexadiene, bicyclo[2,2,1]heptadiene, cycloheptatriene, cyclooctatetraene, methylene-cyclobutane and 1,3-dimethylene-cyclobutane. The reactivities of all these compounds except cyclohexene conform to a logical pattern. The unexpectedly low reactivity of cyclohexene remains unexplained. Reactivity of 1,3-dimethylene-cyclobutane permits calculation of the β parameter in a "stretched" butadiene. It was found that $\beta_{2,11}/\beta_{1,29} = 0.124$. Some hydrogen abstraction reactions are discussed and the pertinent relative rate constants of hydrogen abstraction by methyl radicals are tabulated.

Pursuing our studies of methyl radical addition to olefinic compounds, we recently determined the rate constants of addition to a series of cyclic olefins, dienes and polyenes, with intention of investigating the effects of strain on the reactivity of these reagents. The investigated reactions were carried out in isoöctane solution at 65°. Methyl radicals were generated by a thermal decomposition of acetyl peroxide and the standard experimental technique, described, in a paper by Buckley and Szwarc,¹ was used in these studies. The results were obtained in the form of k_2/k_1 , where the subscripts refer to reactions 2 and 1, respectively





Experimental Results

The experimental results obtained in the course of these studies are summarized in Table I which gives the relative rate constants of methyl radical addition (k_2/k_1) as well as the relative rate constants of α -hydrogen abstraction (k_3/k_1). The investigated cyclic monoölefins were obtained commercially and purified through distillation. Cyclopentadiene was prepared from the respective dimer, and after careful distillation the resulting product was immediately diluted with isoöctane and used for the determination of methyl affinity. Cyclohexadiene-1,3 was prepared by the method described in "Organic Synthesis," and after distillation it was also immediately diluted with isoöctane and then stored in the cold. Cyclohexadiene-1,4 and cyclooctatetraene were commercial products (Aldrich Chemical Co.) repurified before being used. Bicyclo[2,2,1]heptadiene and cycloheptatriene were kindly offered to us by Shell Development Co., and the values for respective k_2/k_1 's were corrected in order to account for the presence of small amounts of impurities. Fortunately, these corrections are very small and therefore they cannot affect our basic conclusions. Norbornene was obtained from Dr. Winstein, whom we thank for this gift. Methylene-cyclobutane was obtained from Aldrich Chemicals and 1,3-dimethylene-cyclobutane was kindly provided by Dr. V. A. Engelhardt of the du Pont Co.

(1) R. P. Buckley and M. Szwarc, *Proc. Roy. Soc. (London)*, **A240**, 396 (1957).

Discussion

The results quoted in Table I show that methyl affinities of cyclic mono-olefins are similar to those found for 2-butenes,¹ cyclohexene being, however, an exception. The methyl affinity (k_2/k_1) of the latter olefin is substantially lower than that of the remaining compounds. Apparently this observation is general and not restricted to the specific case of methyl radical addition. Indeed, Kharasch, *et al.*² found that the addition of CCl_3 radicals proceeds 3 times faster with cyclopentene than with cyclohexene.

The gradation of reactivities in the series of cyclic mono-olefins seems to be correlated with their heats of hydrogenation as shown in Fig. 1. Although this correlation is interesting, it remains to be seen whether it is meaningful. One usually expects that the rate of an exothermic reaction increases with increasing exothermicity. However, in the case of cyclic olefins, the *higher* exothermicity of hydrogenation is associated with the *slower* rate of addition. On the other hand, it should be kept in mind that the heat of hydrogenation is not equal to the heat of radical addition and, as a matter of fact, an increase in one entity need not necessarily be reflected by an increase in the other. The fact that the rate of addition to cyclohexene as well as the rate of H abstraction from this compound are both unusually low might indicate a very unfavorable strain in  and in  radicals.

The reactivities of conjugated cyclic di-olefins show that 1,3-cyclohexadiene is more than twice as reactive as cyclopentadiene. This trend in the reactivity is confirmed by the change observed in the heats of hydrogenation. Both observations indicate a higher stability of cyclopentadiene than

(2) M. S. Kharasch and M. Sage, *J. Org. Chem.*, **14**, 537 (1949); M. S. Kharasch, E. Simon and W. Nudenberg, *ibid.*, **18**, 328 (1953).

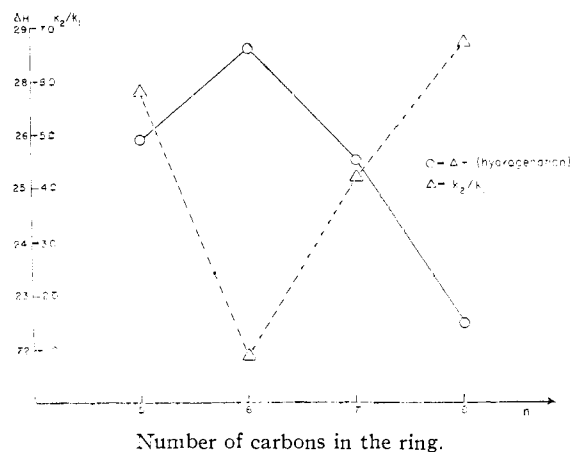


Fig. 1.

of cyclohexadiene, and the possible reason for it may lie in the importance of a Dewar structure in the latter hydrocarbon and its unimportance in the former hydrocarbon. One should point out, however, that cyclopentadiene and cyclohexadiene show similar reactivity in respect to CCl_3 radical addition.² It remains to be seen whether this different behavior is due to some specific effect characteristic for CCl_3 radicals or whether it was caused by the second step of addition which leads to the final product.

The reactivities of the $\text{C}=\text{C}$ bonds in the non-conjugated 1,4-cyclohexadiene are so low that experimentally they could not be determined. Further experimental difficulties arise from the presence in this compound of extraordinarily reactive methylenic groups. Of course, the low reactivity of this compound is in full accord with chemical expectation.

The relatively low reactivities of cycloheptatriene and cyclooctatetraene reflect the lack of complete conjugation resulting from the non-coplanarity of these $\text{C}=\text{C}$ bonds. Nevertheless, the reactivities of these compounds are higher than that of the equivalent number of isolated $\text{C}=\text{C}$ double bonds of the butene-2 type showing that some degree of conjugation does operate in the respective transition states. Inspection of the models suggests that the configuration of cycloheptatriene deviates less from coplanarity than that of cyclooctatetraene, and apparently this is reflected in their methyl affinities.

The reactivity of bicyclo[2,2,1]heptene (norbornene) is relatively high. Actually, this compound also shows high reactivity in other reactions which indicates that one observes a general characteristic of this hydrocarbon. Moreover, its high heat of hydrogenation (see Table I) agrees with its very high methyl affinity. The release of I strain,³ resulting from changing sp_2 configuration into sp_3 , provides an obvious explanation for this phenomenon.

The relatively high reactivity of bicyclo[2,2,1]heptadiene is not surprising in view of the large methyl affinity of norbornene. One might expect that the radical, resulting from addition of methyl radical to this diene, should gain some

(3) H. C. Brown, R. C. Fletcher and R. B. Johannesen, *J. Am. Chem. Soc.*, **72**, 2926 (1950).

TABLE I
METHYL AFFINITIES DETERMINED IN ISO-OCTANE SOLUTION
AT 65°

Hydrocarbon	k_2/k_1	$-\Delta H$ hydrogenation ^b of the first $\text{C}=\text{C}$ bond, kcal./mole	k_3/k_1 , number of reactive H	Number of exp.
<i>cis</i> -Butene-2 ^a	3.8			
<i>trans</i> -Butene-2 ^a	6.7			
Cyclopentene	5.8	26.9	0.81	12
Cyclohexene	0.9	28.6 ^c	.15	8
Cycloheptene	4.2	26.5 ^c	.62	6
Cyclooctene	6.7	23.5 ^c	.40	11
Cyclopentadiene	270	24.0	30	10
Cyclohexadiene- 1,3	665	26.8	51	8
Cyclohexadiene- 1,4	Low	..	High	
Cycloheptatriene	156	(total) 70.5 ^c	17	6
Cyclooctatetraene	81	25.6 ^c	..	6
Bicyclo[2,2,1]heptene				
	50.2	33.13 ^c	<2	6
Bicyclo[2,2,1]hepta- diene	115	35.0 ^c		6

^a These data are taken from ref. 1. ^b Taken from "Modern Aspects of Thermochemistry," by H. A. Skinner, The Royal Institute of Chemistry Monographs No. 3 (1958). ^c Recently redetermined values for heats of hydrogenation of cyclohexene, -heptene and -octene all slightly higher, namely -27.10, -25.85 and -22.98 (R. B. Turner, *et al.*, *J. Am. Chem. Soc.*, **79**, 4116 (1957)).

stability on account of a homo-allyl type resonance. Indeed, some reactions of bicycloheptadiene lead to products which result from 1,4 addition coupled with formation of cyclopropane ring, and this mode of reaction is analogous to the 1,4 addition to butadiene. However, the fact that the methyl affinity of bicyclo[2,2,1]heptadiene is only slightly larger than twice the methyl affinity of norbornene shows that such a resonance is not of great importance. In fact, a conjugation between two $\text{C}=\text{C}$ double bonds diminishes rapidly with the increasing distance separating the respective centers. In bicycloheptadiene the inclination of the p -orbitals seems to increase their overlap, but this gain apparently is offset by the loss of symmetry.

The recent work of Turner, *et al.*,⁴ sheds further light on this point. The higher heat of hydrogenation of the diene as compared with the mono-ene leads to a "negative" resonance energy. The interpretation of the results is complicated by steric factors, but it is difficult to avoid the general conclusion that the conjugation between these double bonds is insignificant. Our work adds a further point, namely, that the conjugation in the resulting radical is also insignificant.

The same conclusion is drawn out by Cristol, Brindell and Reeder⁵ who studied radical addition of p -thiocresol to bicyclo[2,2,1]heptadiene. From analysis of the products they concluded that no homo-allylic radicals are formed as intermediates in this chain process.

The decrease of conjugation rising from increasing the distance separating $\text{C}=\text{C}$ double bonds

(4) R. B. Turner, W. R. Meador and R. E. Winkler, *ibid.*, **79**, 4116 (1957).

(5) S. J. Cristol, G. D. Brindell and J. A. Reeder, *ibid.*, **80**, 4635 (1958).

could be investigated by studying methyl affinity of 1,3-dimethylenecyclobutane. The pertinent data are given in form of graphs of $(k_2/k_1 \text{ exp})^{-1}$ against mole fraction of the investigated compound which are shown in Fig. 2. These graphs permit the calculation¹ of the relative rate constants of addition (k_2/k_1) and of abstraction (k_3/k_1). The methyl affinity of methylenecyclobutane was found to be 42.5, *i.e.*, it differs insignificantly from that of isobutene (methyl affinity = 37¹). This indicates that strain does not affect the reactivity of methylene-cyclobutane and hence apparently neither that of 1,3-dimethylene-cyclobutane. In view of this, a value of $k_2/k_1 = 137$ obtained for the latter diene, which is 60% larger than that expected on the basis of twice the methyl affinity of methylenecyclobutane, seems to be due to the conjugation of the "stretched" butadiene-1,3. The decrease in the conjugation is apparent if one compares the value of 137 with the methyl affinity of ordinary butadiene-1,3 which was found⁶ to be 2015. By using a simple molecular orbital approach and a relation between methyl affinity and localization energy for this type of center,⁷ one may calculate the value of β for the "stretched" C-C bond of 1,3-dimethylene-cyclobutane. One finds in this way that $\beta_{2.11}/\beta_{1.39} = 0.124$ for the C-C distance of 2.11Å. It was assumed in this calculation that the presence of CH₂ groups increases the methyl affinity of dimethylene-cyclobutane by a factor of 2, *i.e.*, that their hyperconjugation effect is similar to that found in isobutene (see ref. 7b). This is, of course, an oversimplification and introduces an uncertainty of about 0.05 in the calculated ratio of $\beta_{2.11}/\beta_{1.39}$.

The possibility of 1,3 π conjugation in 1,3-dimethylenecyclobutane was discussed thoroughly by Roberts and his students.⁸ No evidence for such a conjugation was found in the ultraviolet spectrum of this hydrocarbon. Its heat of hydrogenation was determined by Turner to be -60.03 kcal./mole, *i.e.*, 31.6 kcal./mole larger than that of methylenecyclobutane ($\Delta H = -29.43$). This again does not indicate any appreciable π conjugation. However, determination of the methyl affinity affords a sensitive way of detecting the conjugation operating in the radical. This conjugation is always more pronounced than the conjugation in the parent hydrocarbon. In fact, the small value for β obtained from our results shows that the effect of the conjugation on the heat of hydrogenation will be very small indeed. It also should be pointed out that Roberts estimated the value of β in 1,3-dimethylene-cyclobutane to be 0.33 $\beta_{1.39}$, whereas our estimate is lower.

The very high value of k_3/k_1 obtained for 1,3-dimethylenecyclobutane deserves some comment. The abstraction takes place on a secondary hydrogen and the resulting radical is stabilized by a conjugation with two C=C bonds, all the system

(6) A. Rajbenbach and M. Szwarc, *Proc. Roy. Soc. (London)*, **A251**, 1266 (1959).

(7) (a) M. Szwarc and J. H. Binks, in "Theoretical Organic Chemistry," Kekule Symposium, London, 1958, Butterworth Sci. Publication, p. 262; (b) J. H. Binks and M. Szwarc, *J. Chem. Phys.*, **30**, 1494 (1959).

(8) F. F. Caserio, S. H. Parker, R. Piccolini and J. D. Roberts, *J. Am. Chem. Soc.*, **80**, 5507 (1958).

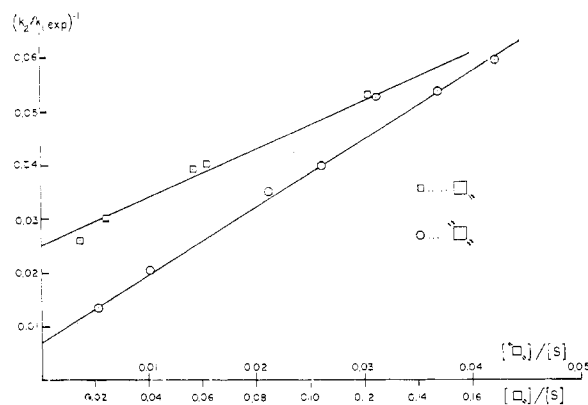


Fig. 2.—□ $k_2/k_1 = 42.5$, $k_3/k_1 = 11.7$; ○ $k_2/k_1 = 137$, $k_3/k_1 = 170$.

being co-planar. Under these circumstances one expects indeed a very high reactivity in the hydrogen abstraction reaction. A comparison of some k_3/k_1 values per active hydrogen is interesting. Table I provides the pertinent data for cyclopentadiene and 1,3-cyclohexadiene, while in ref. 4 one finds the relevant value for 1,4 pentadiene.

Pentadiene-1,4	k_3/k_1 per active hydrogen	20
Cyclopentadiene	k_3/k_1 per active hydrogen	30
1,3-Dimethylene-cyclobutane	k_3/k_1 per active hydrogen	42.5
1,3-Cyclohexadiene	k_3/k_1 per active hydrogen	51

The free rotation in pentadiene-1,4 reduces the reactivity of the respective C-H's. On the other hand, the reactivities of the respective C-H's are fairly similar in 1,3-dimethylenecyclobutane, cyclopentadiene and in 1,3-cyclohexadiene.

Concluding this report, we again wish to emphasize the strange behavior of cyclohexene for which we have no satisfactory explanation. This behavior cannot be accounted for in terms of Pitzer's strain⁹ (see Table II). On this basis cyclohexene should be *more* reactive than cyclopentene. On

TABLE II
STRAIN ENERGIES OF CYCLIC HYDROCARBONS

Hydrocarbon	Strain energy, kcal./mole	Δ
Cyclopentane	9.2	+1.0
Cyclopentene	8.2	
Cyclopentadiene	7.0	+1.2
Cyclohexane (chair)	0.0	-1.5
Cyclohexene	1.5	-2.5
Cyclohexadiene (1,3)	4.0	

the other hand, the strain may account satisfactorily for the greater reactivity of cyclohexadiene as compared with cyclopentadiene.

It was reported by Shine and Slagle¹⁰ that acetyl peroxide reacts abnormally with cyclohexene. Some products, isolated by these workers from the reaction mixture, indicate that CH₃COO radicals add to the C=C double bond of cyclohexene. We confirm that some CO₂ is "lost" in the decomposition of acetyl peroxide proceeding in pure

(9) K. S. Pitzer, *Science*, **101**, 672 (1945).

(10) H. J. Shine and J. R. Slagle, *J. Am. Chem. Soc.*, **81**, 6309 (1959); see also paper presented by Dr. Martin at A.C.S. National Meeting, New York, Sept., 1960.

cyclohexene solution, although no appreciable "loss" was observed in 10 or 20 mole % solution of this compound in isooctane. Moreover, the behavior observed by Shine and Slagle should increase the apparent methyl affinity of cyclo-

hexene and hence obviously this cannot account at all for the observed low value of k_2/k_1 .

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY COLLEGE OF FORESTRY AT SYRACUSE UNIVERSITY, SYRACUSE 10, NEW YORK]

Methyl Affinities of Some Compounds Related to Acrylates and Acrylonitriles. Reactivities of Conjugated Systems Involving Atoms Other Than Carbon

BY L. HERK, A. STEFANI AND M. SZWARC

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Methyl affinities of the following monomers were investigated: methyl acrylate, methyl methacrylate, methyl crotonate, methyl β,β -dimethylacrylate, acrylonitrile, methacrylonitrile, crotononitrile, β,β -dimethylacrylonitrile, methyl vinyl ketone, vinylacetylene and 1-cyanocyclopentene. The high values of methyl affinities found for some of these compounds are discussed in terms of electron-withdrawing capacity of the $-\text{C}=\text{O}$, $-\text{C}\equiv\text{N}$ and $-\text{C}\equiv\text{CH}$ groups. The steric "blocking" effects were noticed in those monomers which had substituents on their β -carbons. The data demonstrate that the methyl radical addition to the hetero-atoms is about one hundredth as fast as the addition to the C center.

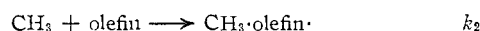
In this communication we report the results of our studies of methyl affinities, *i.e.* the relative rate constants of methyl radical addition of compounds related to acrylates and acrylonitriles. The purpose of this investigation was to find out to what extent the reactivity of a $\text{C}=\text{C}$ double bond is changed as a result of its conjugation to a $\text{C}=\text{O}$, $\text{C}\equiv\text{N}$ or $\text{C}\equiv\text{C}$ group and to discuss the plausible explanations for such changes.

Experimental

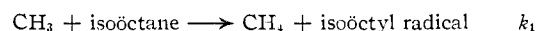
The additions of methyl radicals to these various compounds were investigated: vinyl methyl ketone, methyl acrylate, methyl methacrylate, methyl crotonate, methyl β,β -dimethylacrylate, acrylonitrile, methacrylonitrile, crotononitrile, β,β -dimethylacrylonitrile, 1-cyanocyclopentene and vinylacetylene. Most of these compounds were acquired commercially, and only a few of them had to be prepared. Methyl crotonate was prepared from the corresponding acyl chloride; methyl β,β -dimethylacrylate was obtained by esterification of the commercially available acid; β,β -dimethylacrylonitrile was prepared from isobutyraldehyde according to the method described by Fr. de Laet.¹ Finally, a sample of 1-cyanocyclopentene was kindly offered to us by Dr. Schmitt, its preparation being given in G. Schmitt, Ph. D. Thesis, Syracuse (1960). All the compounds were purified before being used, and the degree of their purity was checked by gas chromatography and found to be better than 99%. β,β -dimethylacrylonitrile being the only exception. Gas chromatography revealed that the last compound contained about 8% of some unknown impurity, although its physical constants checked excellently with those reported in the original paper.

The sample of crotononitrile, which was acquired from K. et K. Laboratories, was separated by distillation into two fractions. In each fraction the presence of two components was revealed by gas chromatography, and these were assumed to be the respective *cis*- and *trans*-isomers. The negligible difference in their boiling points and the identical patterns of their mass spectra added to this contention. From the areas of the chromatography peaks it was calculated that the proportion of the isomers in the first fraction is 67:33 and that in the second amounts to 45:55. Methyl affinities of both fractions were found to be identical (see Table I), and this reassures us that we deal here with isomers. This is even more gratifying since methyl affinities of fumaro- and maleo-nitriles were also found to be identical.²

The usual technique was applied in determining methyl affinities.³ Actually, what is determined experimentally is the k_2/k_1 ratio where k_2 is the rate constant of the investigated process



while k_1 refers to the abstraction of hydrogen from isooctane which was used as a solvent in all these experiments, *i.e.*



Methyl radicals were produced by decomposition of acetyl peroxide, and all the reported experiments were carried out at 65°.

Results

The experimental results are summarized in Table I. In calculation of the averages the values given with the question mark were omitted. The addition of methyl radicals to methyl β,β -dimethylacrylate, β,β -dimethylacrylonitrile and to 1-cyanocyclopentene proceeds simultaneously with hydrogen abstraction from the substrate. In such cases the proper k_2/k_1 value is given by the intercept of the plot of $(k_2/k_1)_{\text{exp}}^{-1}$ versus (mole fraction of substrate)/(mole fraction of solvent). These plots, shown in Fig. 1, give straight lines,³ and their slopes determine the ratios of the rate constant of the hydrogen abstraction (k_3) to the rate constant of the addition (k_2). The relevant results are quoted in the respective figures.

It should be pointed out that the addition of methyl radicals to methyl vinyl ketone, methyl acrylate and methacrylate, as well as to acrylonitrile and methacrylonitrile, may be followed by polymerization of these monomers. No formation of polymer was observed in the respective experiments. Moreover, had such a polymerization proceeded to a considerable extent, the corresponding k_2/k_1 values would decrease with increasing mole % of the monomer. Inspection of Table I shows that this is not the case. Apparently the dilution of the monomers is too high to permit any appreciable polymerization.

(1) Fr. de Laet, *Bull. soc. chim. Belg.*, **38**, 163 (1929).

(2) A. Bader, R. P. Buckley, F. Leavitt and M. Szwarc, *J. Am. Chem. Soc.*, **79**, 5621 (1957).

(3) R. P. Buckley and M. Szwarc, *Proc. Soc. (London)*, **A240**, 396 (1957).