cyclohexene solution, although no appreciable "loss" was observed in 10 or 20 mole % solution of this compound in isoöctane. 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

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 —C=O, —C≡N and —C≡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 C=C double bond is changed as a result of its conjugation to a C=O, C≡N or C≡C group and to discuss the plausible explanations for such changes.
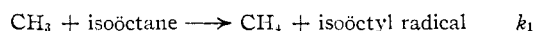
Experimental

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 give 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.etK. Laboratories, was separated by distillation in 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

$$CH_3 + \text{olefin} \longrightarrow CH_3\cdot\text{olefin}\cdot \qquad k_2$$
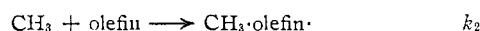
while k_1 refers to the abstraction of hydrogen from isoöctane which was used as a solvent in all these experiments, *i.e.*

$$CH_3 + \text{isoöctane} \longrightarrow CH_4 + \text{isoöctyl radical} \qquad k_1$$

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).

TABLE I

METHYL AFFINITIES (k_2/k_1), DETERMINED IN ISOÖCTANE SOLUTION AT 65°

Investigated compound	Mole %	k_2/k_1
Methyl vinyl ketone	0.15	1925
	.19	2010
	.30	1760
	Av.	1900 ± 75
Methyl acrylate	.030	798(?)
	.061	1005
	.091	1085
	.121	1005
	.151	1030
	Av.	1030 ± 35
Methyl methacrylate	.030	1440
	.060	2060(?)
	.091	1540
	.121	1390
	.151	1390
	Av.	1440 ± 65
Methyl crotonate (5% cis-, 95% trans-)	0.77	69.6
	1.53	67.9
	2.29	65.3
	3.04	67.7
	Av.	67.6 ± 1.0
Methyl β,β-dimethylacrylate	1.34	10.8
	2.68	9.8
	4.00	8.5
	5.32	8.3
	6.63	7.7
	Extrapd. to 0%	11.9
Acrylonitrile	0.024	1710
	.048	1690
	.073	1740
	.097	1815
	.121	1700
	Av.	1730 ± 50
Methacrylonitrile	.024	2190
	.048	2265
	.073	2070
	.097	1990
	.121	2100
	Av.	2120 ± 95
Crotononitrile (cut 67:33)	.76	72.9
	1.14	72.9
	1.52	72.1
	1.90	71.4
	Av.	72.3 ± 0.3
Crotononitrile (cut 45:55)	0.40	74.8
	1.20	73.5
	1.59	74.6
	1.99	75.6
	Av.	74.4 ± 0.4
β,β-Dimethylacrylonitrile (92% pure)	2.3	18.2
	4.6	14.5
	6.8	12.9
	9.0	10.4
	11.2	9.1
	Extrapd. to 0%	23.5

1-Cyanocyclopentene	0.33	191
	0.67	170
	1.00	148
	1.33	134
	1.66	114
	Extrapd. to 0%	224
Vinylacetylene	0.072	2280
	.091	2080
	.119	2420
	.158	2260
	Av.	2260 ± 80

Discussion

An interesting point emerges from an inspection of the data given in Table I. All the investigated monomers, which do not possess substituents on the β-carbon, have *higher* methyl affinities than styrene or butadiene. This point was emphasized in a previous communication from this Laboratory,[4] in which methyl affinities of methyl
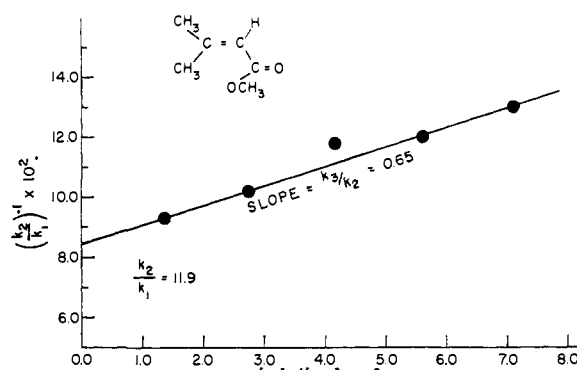

Fig. 1a.

methacrylate and acrylonitrile were reported. The value for methyl affinity of the former monomer is reconfirmed; however, we believe that the value reported then for the latter monomer was too low; the one given in Table I is more reliable.

The high reactivities of the investigated monomers are shown clearly in Table II in which their methyl affinities are compared to that of styrene taken as unity. In the same table we list also the

TABLE II

Monomer	For CH₃ addition at 65° k_2/k_1, styrene CH₃-addition	For Ph addition at 25°[a] k_{add}/k_{add}, styrene Ph-addition
Styrene[b]	1.00	1.00
Butadiene-1,3[c]	2 × 1.27	..
Methyl acrylate	1.30	0.92–0.93
Methyl methacrylate	1.81	1.25–1.26
Acrylonitrile	2.17	1.16
Methacrylonitrile	2.67	1.35
Methyl vinyl ketone	2.26	..
Vinylacetylene	2.84	..

[a] From a paper by S. C. Dickerman, I. S. Megau and M. M. Skoultchi, 81, 2270 (1959). [b] Reported by M. Leavitt, M. Levy, M. Szwarc and V. Stannet, 77, 5493 (1955). [c] Reported by A. Rajbenbach and M. Szwarc, Proc. Roy. Soc., (London), A251, 1266 (1959).

(4) M. Szwarc, J. Polymer Sci., 16, 367 (1955).
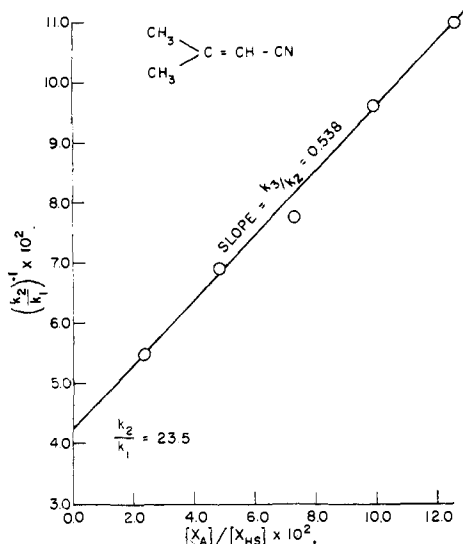
Fig. 1b.

Fig. 1c.

relative rates of addition of phenyl radicals,[5] again compared to that of styrene. It is obvious that similar trends are observed in both series of reactions.

The high reactivity of styrene and of butadiene results from a considerable gain in resonance energy of the resulting radicals. Of course, the resonance energies of radicals derived from the remaining monomers listed in Table II cannot be as high as that of benzyl or allyl radical, and hence another factor must be of importance in determining their reactivity. We suggest that the electron withdrawing power of the conjugated substituent is of at least as great importance in determining the reactivity of the relevant monomer toward methyl or phenyl radicals as is its effect upon the resonance energy of the resulting radical. Indeed, the increase in methyl affinities resulting from electron withdrawing action of some substituents was noticed previously,[6] and it has been discussed in terms of changes affecting the repulsive forces operating in the transition state.

Correlation of the observed methyl affinities to other characteristic properties of the substituents (—C=O, —C≡N, —C≡C, etc.) is complicated by the simultaneous operation of resonance effects and electron-withdrawing effects. The closest correlation is expected with σ_p' which applies to reactions of anilines and phenols. For example, these σ values are +0.68 and +0.87 for p-COOEt and p-COCH$_3$, respectively,[7] and the increase in σ compares well with the increase in methyl affinities of methyl vinyl ketone in respect to methyl acrylate. In both monomers one deals with the same C=C—C=O conjugated system; however, the more strongly electron donating OCH$_3$ group reduces the reactivity of methyl acrylate to an extent greater than that by which the weakly electron donating CH$_3$ group affects the reactivity of vinyl methyl ketone. On the other hand, even

(5) S. C. Dickerman, I. S. Megau and M. M. Skoultchi, J. Am. Chem. Soc., 81, 2270 (1959).

(6) R. P. Buckley and M. Szwarc, ibid., 78, 5696 (1956).

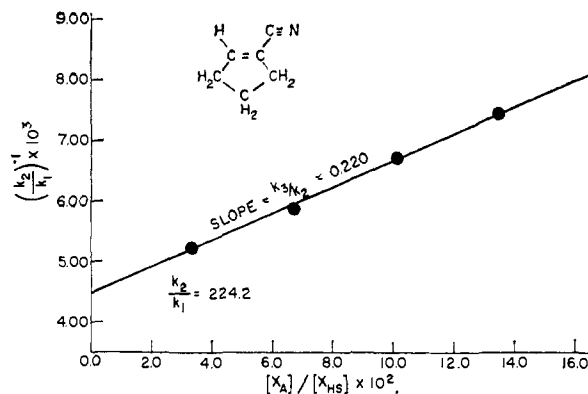(7) J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1956.

those σ values are not suitable to gauge the reactivity when different conjugated systems are compared. For example, vinyl methyl ketone adds methyl radicals more readily than acrylonitrile, although the respective σ_p' values[7] are +0.87 and +1.00. The example of vinylacetylene is most instructive. The powerful electron-withdrawing tendency of —C≡CH group makes this monomer the most reactive in the whole series, as is expected on the basis of this discussion. Although no data are available on the position of the reactive center, we feel strongly that the addition involves the *CH$_2$=CH— center and not the *CH≡ C— center.

Substitution of methyl group on the α-carbon of the vinyl group increases the reactivity of the respective monomer, the effect being due to hyperconjugation operating in the radical. It is interesting to compare the reactivity ratios of a methylated and a non-methylated substrate, which are

Pair	CH$_3$-addition	Ph-addition
$\dfrac{\alpha\text{-Methylstyrene}}{\text{Styrene}}$	1.17	..
$\dfrac{\text{Methyl methacrylate}}{\text{Methyl acrylate}}$	1.40	1.36
$\dfrac{\text{Methacrylonitrile}}{\text{Acrylonitrile}}$	1.22	1.17

A methyl group located on a β-carbon of the vinyl group exerts a "blocking" effect which, of course, is expected to be even larger whenever two methyl groups are introduced into that position. This, indeed, is revealed by the data listed in Table I. The "blocking" effect of one methyl group decreases the reactivity in the acrylate series by a factor of 15 (see methyl affinity of methyl crotonate), and in the acrylonitrile series by nearly a factor of 23 (see methyl affinity of crotononitrile). These effects are larger than those observed in other series of substrates,[8] where the "blocking" effect appears to introduce a factor of only 9 ± 2 in the respective reactivity. It is tempting to attribute these large "blocking" effects to both steric and electron donating influences. The latter effects seem to be magnified in the presently investigated monomers because they act as effective electron sinks.

(8) M. Szwarc and J. H. Binks, "Theoretical Organic Chemistry," Kekule Meeting, London, 1958, Butterworth Publication, 1959, p. 262.

Introduction of two methyl groups increases the "blocking" effect to a factor of 90 (for methyl β,β-dimethylacrylate) and of 75 (for β,β-dimethylacrylonitrile). Only two examples of such a "blocking" have been reported,[8] namely, this in 1,1,4,4-tetramethylbutadiene which amounts to a factor of 75 and that in 9,9-dimethylfulvene reducing the reactivity by a factor of 72.

The examples of methyl β,β-dimethylacrylate and β,β-dimethylacrylonitrile serve to show that the addition of methyl radicals to hetero-atoms is negligible if any. Such an addition must be slower by a factor greater than 100 than the addition to a carbon center. The reluctance of methyl radical to add to a hetero-atom was pointed out in previous publications from this Laboratory[8] and it was attributed to the increasing repulsion due to the presence of a lone pair of electrons.

Methyl affinity of 1-cyanocyclopentene seems to be too high. At the same time one notices that the rate of hydrogen abstraction from this compound also appears to be unduly high. No explanation is offered to account for these observations.

Structure and Reactivity in the Radiolysis of Ketones

BY J. N. PITTS, JR., AND A. D. OSBORNE

A series of six ketones has been subjected to radiolysis at 25° with 3 Mev. gamma rays from the van der Graaf accelerator of the Shell Development Company. The compounds were: methyl n-propyl, methyl n-butyl, methyl n-amyl, methyl cyclopropyl, dicyclopropyl and methyl propenyl ketones. Detailed product analysis has been carried out and G-values for the various products are reported. With methyl n-propyl, methyl n-butyl and methyl n-amyl ketones degradation into radicals and an intramolecular formation of acetone and olefin are the main processes. Thus for methyl n-propyl ketone $G(CO) = 0.38$, $G(CH_4) = 0.42$, $G(C_3H_8) = 0.36$, $G(C_2H_4) = 0.15$ and $G(\text{acetone}) = 0.13$. Methyl n-propyl ketone also gives rise to appreciable amounts of acetaldehyde ($G = 0.12$) and propylene ($G = 0.09$). With the cyclopropyl and unsaturated compound photorearrangement to an isomer is the main process, and there is little gaseous product. Dicyclopropyl ketone is particularly stable toward radiolysis. ($\Sigma G(\text{gaseous product}) = 0.36$ compared to 1.88 for methyl n-propyl ketone.)

Introduction

Radiolysis studies with acetone, methyl ethyl ketone and diethyl ketone have been undertaken by Ausloos and Paulson[1] who found that the formation of the major products could be explained on the basis of well known radical reactions. Experiments with scavengers indicated that most of the methyl radicals became thermalized before abstracting hydrogen. A few experiments with methyl n-propyl and methyl n-butyl ketones gave appreciably lower yields of carbon monoxide. Thus, they obtained values of 0.48 and 0.40, respectively, for $G(CO)$ as compared with 0.74 for the lower ketones. This effect is analogous to well recognized results of photochemical studies; ketones having gamma hydrogen atoms give appreciably lower quantum yields of carbon monoxide than for example acetone or diethyl ketone.[2,3] Recently the effect of added acetone on hydrogen formation in the radiolysis of 2-propanol has been investigated in detail,[4] and it was concluded that acetone is an efficient trap for hydrogen atoms formed in the photolysis of this substance.

A more detailed examination of the radiolysis of ketones having gamma hydrogen atoms has been undertaken. In order to obtain a more comprehensive picture of the effects of molecular structure on the modes of decomposition by radiolysis, we have included an α,β-unsaturated ketone and two ketones containing cyclopropyl groups. The gas phase photochemistry of these substances has already been investigated in these laboratories.[5-7]

Experimental

The six ketones were purified by preparative GL-Chromatography using the Beckman Megachrom with a silicone oil stationary phase. This instrument will handle 20 ml. samples, which makes it possible to prepare appreciable quantities of material of high purity. The purified compounds were chromatographed on a conventional column with a Ucon Polar stationary phase to check their purity and to provide reference chromatograms for comparison with the irradiated material. Dicyclopropyl ketone still showed an impurity of 2-3% which is not resolved from dicyclopropyl ketone by a silicone column. The other ketones had a total impurity of less than 1/2%.

Two one ml. samples of each compound were weighed and distilled under vacuum into 10 mm. diameter sample tubes having a glass break-off seal. In addition, two samples each of methyl n-propyl, methyl n-butyl and methyl n-amyl ketones were prepared and iodine added to a concentration of approximately 5×10^{-3} M. Three of these samples with iodine were kept as blanks (one of each ketone), and the rest of the samples were shipped to the Shell Development Company at Emeryville, California, for irradiation with 3Mev. van der Graaf Bremsstrahlung. Each tube was irradiated for 15 minutes at 25° at a dose rate of 1.46×10^8 rads./hour (1 rad. = 100 ergs/g.).

Primary separation of products for analysis was carried out under vacuum using a solid nitrogen trap, a LeRoy-Ward still, a mercury diffusion pump and a Toepler pump with calibrated gas buret. In each case the break-off seal was broken with a glass enclosed piece of iron, which could be manipulated with a magnet external to the apparatus. The sample was immersed in a bath of Dry Ice

(1) P. Ausloos and J. F. Paulson, *J. Am. Chem. Soc.*, **80**, 5117 (1954).

(2) W. Davis, Jr., and W. A. Noyes, Jr., *ibid.*, **69**, 2153 (1947).

(3) For a review see J. N. Pitts, Jr., *J. Chem. Educ.*, **34**, 112 (1957).

(4) J. D. Strong and J. G. Burr, *J. Am. Chem. Soc.*, **81**, 775 (1959).

(5) R. S. Tolberg and J. N. Pitts, Jr., *ibid.*, **80**, 1304 (1958).

(6) J. N. Pitts, Jr., and I. Norman, *ibid.*, **76**, 4815 (1954).

(7) J. N. Pitts, Jr., and R. S. Woolfolk, Abstracts, 133rd Meeting Am. Chem. Soc., April 1958, p. 4-Q.