Table I. ^{13}C Chemical Shifts[a] and Assignments

	C2	C4	C5	C6	C8	C9	C1′	C2′	C3′	C4′	C5′
Formycin A	151.6	138.7	123.0	151.6		143.7	78.3	75.5	72.7	86.3	62.8
Adenosine	152.5	149.1	119.4	156.2	140.1		88.1	73.6	70.8	86.0	61.8
8-Azaadenosine	156.1	148.8	124.1	156.7			89.7	72.9	70.7	86.2	61.8
Formycin B	143.3	136.7	128.0	153.6		144.7	77.7	74.9	72.1	85.7	62.5
Inosine[c]	148.2	146.0	124.5	156.7	138.9		87.9	74.3	70.4	85.8	61.4
4-Mercapto-1*H*-pyrazolo-[3,4-*d*]pyrimidine[b]	146.3 (C6)	148.8 (C8)	116.8 (C9)	179.4 (C4)	C7 = 136.4 (C3)						
6-Azauridine	148.7	156.8	136.6				89.7	72.6	70.6	84.9	62.3
Uridine	151.2	163.8	102.2	141.6			88.3	74.0	70.3	85.2	61.3
6-Azathymine	149.7	157.5	142.7		CH_3 = 15.9						
Thymine	151.6	165.0	107.8	137.8	CH_3 = 11.9						
Thymidine	150.5	163.8	109.5	136.2	CH_3 = 12.3		83.9	39.5	70.5	87.3	61.4

[a] Values given are in ppm from TMS. DMSO-d_6 was used as solvent and as an internal reference, and the values were changed to a TMS scale using δ(TMS–DMSO-d_6) = 39.5 ppm. The formycin A and formycin B were a gift from Dr. H. Umezawa. The 8-azaadenosine was a gift from Dr. J. A. Montgomery. [b] The assignments in parentheses correspond to the IUPAC numbering system. In the table the chemical shifts are listed under the corresponding adenine carbons for comparison. [c] These values are from ref 2a and were converted to a TMS scale using δ(TMS–benzene) = 127.6 ppm.

pyrazole showed broadened resonances that narrowed with increasing temperature. The lines narrowed with the addition of H_2O or D_2O and became very narrow with the addition of small amounts of acid or base. These data are consistent with the observation that the broadening results from prototropic tautomerization. With these compounds a careful study of the concentration and solvent dependence of the line widths must be completed to determine the effect of self association[9] and interaction with the solvent.[9,10] The only other compound studied that exhibited the pronounced line broadening was 4-mercapto-1*H*-pyrazolo[3,4-*d*]pyrimidine. This compound is a better model for the formycin ring system than the indazoles and like the formycins it has two sites where tautomeric equilibria may be important.

The ^{13}C spectra of 8-azaadenosine, 6-azathymine, and 6-azauridine all exhibited narrow resonances. The chemical shifts of these compounds (Table I) further illustrate the large perturbations of the electronic structure of the ring system when a nitrogen atom is introduced, as has been noted in other compounds.[11] This perturbation of the electronic structure of the nucleosides may have a significant effect on the presence of the rare tautomeric forms of the nucleosides. Theoretical calculations (G. P. Ceasar and J. Greene, personal communication) have shown that the change in the ring structure in going from adenine to formycin A can have significant effects on the relative stabilities of the amino and imino tautomers.[12] The present experiments provide convincing evidence that prototropic tautomerization is an important consideration in the nucleoside antibiotics formycin A and formycin B.

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Base and Acid Catalyzed Protonation of the Acrylate Radical Dianion at the β Position. Spectral and Kinetic Evidence

Sir:

We report the results of a spectral and kinetic study of the reaction of the hydrated electron, e_{aq}^-, with acrylic acid and acrylate ion and of the subsequent protonation reactions of these radical anions. Data presented below show that in neutral aqueous solution the acrylate radical dianion undergoes protonation on the carboxyl group. In alkaline solution, the dianion radical undergoes protonation at the β carbon. *The latter protonation reaction is catalyzed by hydroxide ions.* The radical anions of acrylamide and methacrylamide were found[1] to undergo protonation at the carboxamide group in weakly acidic solution and at the β-carbon atom in alkaline solution. However, the latter protonation reaction was *not* catalyzed by OH^- ions.

Details of the pulse radiolytic experimental conditions used are described elsewhere.[2] Acrylic acid (Matheson Coleman and Bell or Eastman) was purified by recrystallizing from the melt, vacuum distilled under nitrogen, and recrystallized from the melt a second time. $G(e_{aq}^-) = 2.8$ was used to derive extinction coefficients.

The specific rates of reaction[3] of e_{aq}^- with acrylic acid and acrylate ion are respectively (2.2 ± 0.1) ×

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(2) M. Simic, P. Neta, and E. Hayon, *J. Phys. Chem.*, 73, 3794 (1969); J. P. Keene, E. D. Black, and E. Hayon, *Rev. Sci. Instrum.*, 40, 1199 (1969).
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10^{10} and $(5.3 \pm 0.5) \times 10^9$ M^{-1} sec^{-1}. The protonated form of the acrylate radical anion has[4] λ_{max} 260 nm and ϵ_{260} 7.7×10^3 M^{-1} cm^{-1} and is tentatively assigned the structure CH_2⋯CH⋯$C(OH)$⋯$O\cdot^-$. This radical decays by first-order kinetics with $k = (4.0 \pm 0.5) \times 10^4$ sec^{-1}, to give a transient species A. On ionization of this radical, $pK_a = 7.0 \pm 0.1$ (ref 4), the spectrum at pH 9.5 of the radical dianion CH_2⋯CH⋯$CO_2\cdot^{2-}$ has λ_{max} 285 nm and ϵ_{285} 9.7×10^3 M^{-1} cm^{-1} (see Figure 1a). This radical decays by a first-order process with $k = (7.7 \pm 0.6) \times 10^4$ sec^{-1} at pH 9.5 and $\mu = 0.01$ M, to give the same transient species, A. Species A has completely different spectral characteristics, with λ_{max} 330 nm and ϵ_{330} 1.1×10^3 M^{-1} cm^{-1}. At pH 12.0, the only transient observed with our time resolution of ~0.1 μsec is identical with that produced at pH 9.5 by the decay of the CH_2⋯CH⋯$CO_2\cdot^{2-}$ radical dianion (see Figure 1a). Species A decays at both pH 9.5 and 12.0 by second-order kinetics with $2k = (1.0 \pm 0.2) \times 10^9$ M^{-1} sec^{-1}.

The physical parameters of species A are in excellent agreement with the previously reported[5] absorption spectrum of the $CH_3\dot{C}HCOO^-$ radical produced by the reaction

$$e_{aq}^- + CH_3CHClCOO^- \longrightarrow CH_3\dot{C}HCOO^- + Cl^-$$

More recent esr work on the interaction of e_{aq}^- with acrylate ion in a flow system at 20° reported[6] $CH_3\dot{C}H$-COO^- as the only observable radical. These workers were apparently unable to observe the $(CH_2{=}CHCOO^-)^-$ radical owing to its relatively short lifetime.

The protonation of the dianion CH_2⋯CH⋯$CO_2\cdot^{2-}$ at the β position was found to be catalyzed by hydroxide ions (see Figure 1 and Table I) with $k = (7.7 \pm 0.3) \times 10^8$ M^{-1} sec^{-1} to give the $CH_3\dot{C}HCOO^-$ radical. In the pH range 7.8–9.5 (*i.e.*, at low hydroxide ion concentrations), this protonation reaction is catalyzed by NH_3, NH_4^+, $H_2PO_4^-$ (not HPO_4^{2-}), $HP_2O_7^{3-}$, and borate buffers; see Table I. This reaction is thus subject to general base and general acid catalysis. Weak acids would appear to favor protonation at the β-carbon atom in contrast to protonation on oxygen by H_3O^+. Since the corresponding acrylamide radical anion CH_2⋯CH⋯$CONH_2\cdot^-$ does not undergo catalysis of protonation by OH^- ions, the ionized carboxyl group in acrylate presumably affects the interaction with OH^- and the buffers examined.

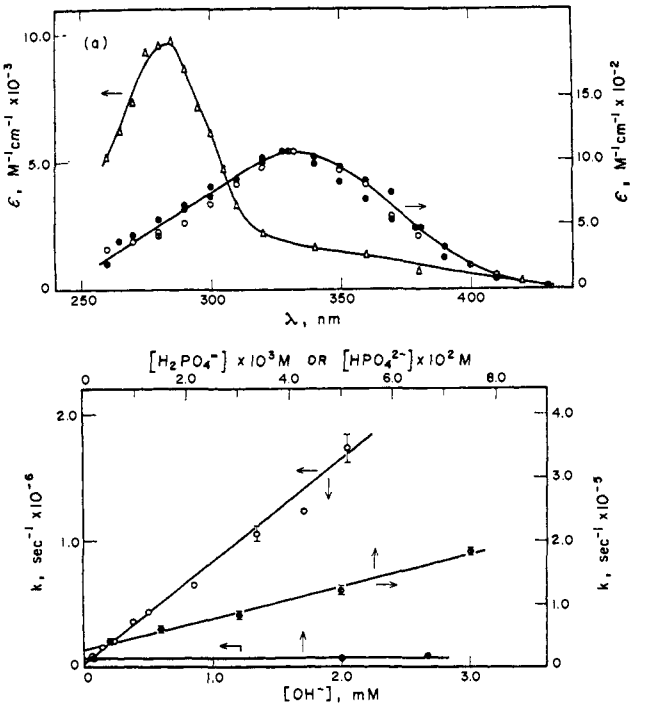

Figure 1. (a) Transient absorption spectra resulting from the action of e_{aq}^- on acrylate ion in air-free aqueous 1.0 M *tert*-butyl alcohol solutions at pH 10.0 (2 mM acrylate, ~8 krads/pulse, OD read at "zero time," Δ, and at 20 μsec after the electron pulse at pH 10.0, ●) and at pH 12.0 (5 mM acrylate, ~19 krads/pulse, read at "zero time," ⊗). Transient spectrum of the $CH_3\dot{C}HCOO^-$ radical, ⊙, produced from the action of e_{aq}^- on α-chloropropionic acid (50 mM, pH 9.2, 1.0 M *t*-BuOH, ~19 krads/pulse). (b) Dependence of the pseudo-first-order rate of decay of the acrylate radical dianion (5 mM acrylate, 1.0 M *t*-BuOH, dose ~8 krads/pulse) at 285 nm upon the concentrations of OH^- ions (⊙), $H_2PO_4^-$ (⊗), and $HPO_4^{2-}\cdot$ ions (●).

Table I. Second Order Rate Constants for the Protonation of the Acrylate Radical Dianion in Water by Various Buffers[a]

Buffer	Ionic strength, μ	Rate k, M^{-1} sec^{-1}
OH^-	0.03	$(7.7 \pm 0.3) \times 10^8$
$H_2PO_4^-$	0.22	$(2.0 \pm 0.2) \times 10^7$
HPO_4^{2-}	0.20	$\leq 4.0 \times 10^4$
$HP_2O_7^{3-}$	0.50	$(1.4 \pm 0.1) \times 10^6$
NH_4^+	0.10	$(9.0 \pm 0.5) \times 10^5$
NH_3	0.10	$(2.5 \pm 1.0) \times 10^6$
$B(OH)_4^-$	0.22	$(6.0 \pm 1.5) \times 10^5$
$B(OH)_3$	0.1–0.5	$(3.0 \pm 0.5) \times 10^5$

[a] Determined by following the pseudo-first-order decay of the acrylate radical dianion at 285 nm in presence of various concentrations of the buffers. In the presence of 1 mM buffers, the acrylate radical dianion decays at pH 8.2 with $k = (3.5 \pm 0.5) \times 10^4$ sec^{-1}. See also text and Figure 1.

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Reaction of *S*-(2-Pyridyl) Thioates with Grignard Reagents. A Convenient Method for the Preparation of Ketones

Sir:

Many reports on the synthesis of ketones from organometallic compounds and carboxylic acid derivatives[1] have appeared. The reactions of Grignard

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