Evidence for a New Low-Temperature Methane Formation Pathway upon Coadsorption of Hydrogen with Methyl Iodide on Ni(100) Surfaces

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Recent studies have shown that alkyl iodides adsorbed on transition metals dissociate easily at the C–I bond to yield surface alkyl species.[1-14] Those moieties usually go on to disproportionate to alkanes, olefins (when possible), hydrogen, and carbon, but if hydrogen is present on the surface, most dehydrogenation steps slow down and the reductive elimination of alkyl groups as alkanes becomes the predominant reaction.[15,16] In this communication we report evidence for the occurrence of a third conversion channel when in the presence of large coverages of surface hydrogen by which methyl iodide yields methane directly in one concerted step.

The experiments reported here were done in an ultrahigh vacuum (UHV) stainless steel bell-jar evacuated with a turbomolecular pump to base pressures below 1×10^{-10} Torr and equipped with instrumentation for X-ray photoelectron (XPS) and thermal programmed desorption (TPD) spectroscopies.[1,6] The kinetics of the C–I bond cleavage reaction was measured isothermally using the XPS signal intensity at 620.4 eV;[5,6] the noise level in those experiments was about 50 cps (counts per second), which translates to a coverage close to 20% of saturation. XPS kinetic data were acquired for 240 s, after which TPD spectra were taken using a heating rate of 10 K/s.

TPD experiments indicate that on Ni(100) the presence of surface hydrogen drastically modifies the chemistry of adsorbed methyl iodide. The left panel of Figure 1 shows that both CD_3H and CD_4 are produced from CD_3I in the absence of coadsorbed hydrogen (other than about 5% from background adsorption), but this only happens above 200 K, after the C–I bond has been broken and methyl moieties have formed on the surface.[5,6] The same results are obtained even when the surface is annealed to 160 K before recording the TPD data, which proves that the concentration of methyl surface groups is not depleted after such treatment, and also when hydrogen dosing is done after saturation with methyl iodide. On the other hand, when hydrogen is adsorbed prior to methyl iodide dosing, a new methane desorption peak develops around 150 K, the area of which decreases with increasing annealing temperature (Figure 1, right).

The formation of methane at these low temperatures correlates well with the kinetic behavior of the C–I bond breaking reaction. Our XPS kinetic data for the coadsorption system display two distinct regimes with two clearly different time constants, namely, an initial sudden drop in signal that stops after partial conversion and a slower process that takes place until at C–I bonds are broken (Figure 2). The extent of dissociation reached in the first time interval depends on the temperature of the surface and is related

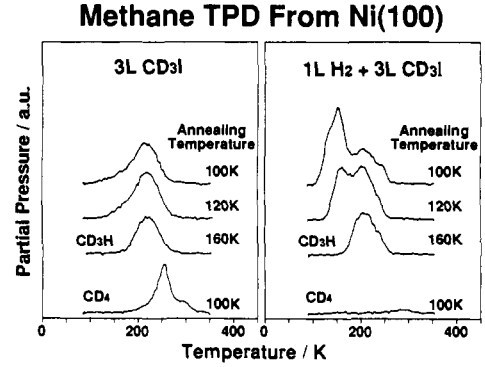

Figure 1. CD_3H and CD_4 TPD spectra obtained after 3 L of CD_3I on Ni(100) by itself (left) and after exposure to 1 L of H_2 (right). The surface was dosed at 90 K in all cases and then annealed to the indicated temperatures before recording the TPD data.

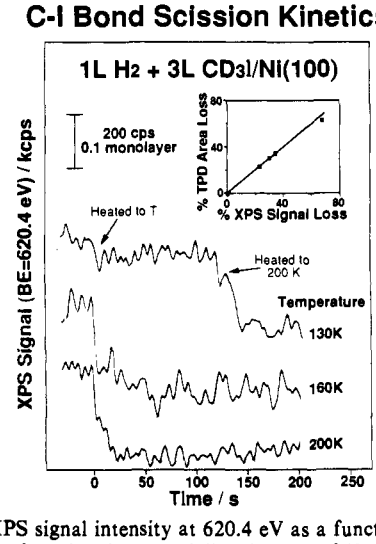

Figure 2. XPS signal intensity at 620.4 eV as a function of time from a Ni(100) surface dosed sequentially with 1 L of H_2 and 3 L of CD_3I at 90 K and then heated to the indicated temperatures. The inset shows the correlation between TPD and XPS signal losses in the first low-temperature reaction.

Table 1. XPS and TPD Results from H_2 + CD_3I Coadsorption on Ni(100)

run	annealing T/K	%I XPS signal loss $\Delta S(T)/\Delta S(200\ K)$ (±5%)	low temperature CD_3H TPD peak area	% CD_3H TPD area loss (±5%)
1	100		3.55	
2	120	23	2.22	23
3	130	30	1.77	31
4	140	34	1.53	35
5	160	67	0	63

to the amount of CD_3H that desorbs after annealing to the same temperatures (Table I and Figure 2, inset). This behavior, which indicates that methyl hydrogenation is not rate limiting, is only observed in the presence of coadsorbed hydrogen; in its absence only one simple exponential decay is seen for each surface temperature.[5,6]

In summary, our data indicates that (1) coadsorbed hydrogen induces fast C–I bond scission in some of the methyl iodide adsorbed on Ni(100), (2) this reaction takes place at temperatures significantly lower than those needed on a clean surface, and (3) the extent of the dissociation reached by this process corresponds to the amount of methane formed at the same temperature. It is clear that the rate-limiting step comprises the scission of the C–I bond, because the rate for that process equals that of the formation of methane. Moreover, the coadsorbed hydrogen is probably directly involved in this step as well, since on clean nickel surfaces molecular dissociation is much slower, and no methane forms below 200 K. These two conclusions lead us to propose

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a concerted mechanism in which hydrogen incorporation takes place as the iodine atom leaves the methyl iodide molecule. It should be pointed out that this step is qualitatively different than that seen on clean surfaces and that even in the presence of surface hydrogen about 30% of the methyl iodide does react following the more conventional pathway where methane desorption is rate limiting.

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Efficient Method for the Preparation of Peptoids [Oligo(N-substituted glycines)] by Submonomer Solid-Phase Synthesis

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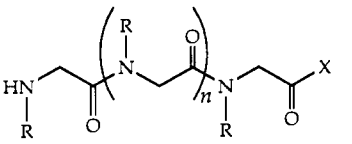
Oligomers of N-substituted glycines, or "peptoids", represent a new class of polymers (Figure 1) that are not found in nature, but are synthetically accessible and have been shown to possess significant biological activity and proteolytic stability.[1] We present here an efficient, automated solid-phase method for the synthesis of oligo(N-substituted glycines) (NSGs) which is general for a wide variety of side-chain substituents and allows the rapid synthesis of molecules of potential therapeutic interest.

The original method[1] for the synthesis of oligomeric NSGs is analogous to standard solid-phase methods for peptide synthesis. Specifically, the carboxylate of N^{α}-Fmoc-protected (and side-chain-protected) NSGs is activated and then coupled to the secondary amino group of the resin-bound peptoid chain. Removal of the Fmoc group is then followed by addition of the next monomer. Thus, oligomeric NSGs have been treated as condensation homopolymers of N-substituted glycine. A disadvantage of this approach, however, is the necessity of preparing suitable quantities of a diverse set of protected N-substituted glycine monomers.

In the method presented here, each N-substituted glycine monomer is assembled from two readily available "submonomers" in the course of extending the NSG polymer (Scheme I). Thus, oligomeric NSGs can also be considered to be alternating condensation copolymers of a haloacetic acid and a primary amine. As in the original method, the direction of polymer synthesis with the submonomers occurs in the carboxy to amino direction. The solid-phase assembly of each monomer, in the course of controlled polymer formation, eliminates the need for N^{α}-protected monomers, as only reactive side-chain functionalities need to be protected. The α-haloacetyl submonomer is common to all cycles of chain extension. Moreover, each RNH_2 submonomer is simpler in structure and many are commercially available; thus, oligo(NSG) synthesis is dramatically simplified.

The preparation of NSG oligomers by the submonomer method[2] in a solid-phase mode has been adapted to a robotic synthesizer.[3] Each cycle of monomer addition (Scheme I) consists of two steps, an acylation step and a nucleophilic displacement step—there is no N^{α}-deprotection step. The first step, acylation of a resin-bound secondary amine with a haloacetic acid,[4] uses a carbodiimide or other suitable carboxylate activation method. A haloacetyl halide could also be used. Acylation of a secondary amine can be difficult, especially when coupling a bulky amino acid. The new process is facilitated by the use of haloacetic acids which, in the presence of a carbodiimide, are potent acylating agents. The second step introduces the side chain by nucleophilic displacement of the halogen (as a resin-bound α-haloacetamide) with an excess of primary amine. The efficiency of the displacement is modulated by the choice of halide (e.g., I > Cl). Protection of carboxyl, thiol, amino, and other reactive side-chain functionalities is required to minimize undesired side reactions. However, the mild reactivity of some side-chain moieties toward displacement or acylation may allow their use without protection (e.g., indole, imidazole, and phenol).



R = side chain
X = NH_2, OH

Figure 1. Representative structure of an oligomeric N-substituted glycine. These polyamide structures differ from polypeptides in that the side chains are substituted on the nitrogen rather than the α-carbon.

Optimization of penta(NSG) synthesis was performed using combinations of chloro-, bromo-, and iodoacetic acids for the haloacetyl submonomer, with both aniline and cyclohexylamine for the RNH_2 submonomer. Bromoacetic acid and iodoacetic acid proved superior to chloroacetic acid in forming penta(*N*-phenylglycine) (79%, 83%, and <5% yields, respectively). All three haloacetyl compounds successfully gave the penta(*N*-cyclohexylglycine) oligomer in >75% yield. However, inclusion of 0.6 M *N*-hydroxybenzotriazole in the acylation reactions[6] yielded <5% of the penta(*N*-cyclohexylglycine) polymer. In further optimization studies, the molar concentration of amine was varied from 0.25 (4.0 equiv) to 2.5 M (40 equiv) for *n*-butylamine, cyclopropylamine, and diphenylethylamine using bromoacetic acid. Pentamers were obtained in >80% yield with *n*-butylamine and cyclopropylamine at concentrations ≥1.0 M and with diphenylethylamine at concentrations ≥2.5 M.

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(2) Oligomer syntheses were performed on a robotic synthesizer.[3] The syntheses were conducted with Rink amide polystyrene resin[7] (50 μmol, substitution level 0.45 mmol/g) to avoid diketopiperazine formation. Acylation reactions were performed by addition of bromoacetic acid (600 μmol, 83 mg) in DMF (0.83 mL), followed by addition of *N,N'*-diisopropylcarbodiimide (660 μmol, 103 μL) in DMF (170 μL). Reaction mixtures were agitated at room temperature for 30 min. Each acylation was repeated once. Displacement reactions were performed by addition of primary amine (2.0 mmol) as 2.5 M solutions in dimethyl sulfoxide (1.0 mL), followed by agitation for 2 h at room temperature. Optimization of displacement reactions was performed by varying amine concentrations from 0.25 to 2.5 M. Side-chain protecting groups were removed, and the oligomer was released from the resin support by treatment of the oligomer-resin with 95% trifluoroacetic acid in water (10 mL) for 20 min at room temperature, followed by filtration, dilution, and lyophilization.

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